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# PARRY'S CYCLOPÆDIA OF PERFUMERY

A HANDBOOK

On the Raw Materials used by the Perfumer, their Origin, Properties, Characters and Analysis, and on other subjects of Theoretical and Scientific Interest to the User of Perfume Materials, and to those who have to Examine and Value such Materials

Checker

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A — L



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## PREFACE

THE need for a scientific work of reference devoted to perfumery and its raw materials has long been felt, and it is hoped that the publication of the present volumes will go some way towards meeting that want.

Formulae for finished perfumes are not dealt with. In the first place, really good formulae are rarely published, and the best of those that are are merely an index to the perfumer, giving him hints as to the direction in which he should experiment. Where such formulae are required they will be found to a more or less unlimited extent in books of a more empirical character.

I have to express my great indebtedness to the following publications and individuals for the kind way, in the case of the former, in which they have allowed me to use them with a free hand, and, in the case of the latter, for so kindly contributing articles which will be found over their respective initials:—

*The Perfumery and Essential Oil Record.*

*The Chemist and Druggist.*

*La Parfumerie Moderne.*

*Les Parfums de France.*

*Messrs. Roure-Bertrand Fils, Bulletin.*

*Messrs. Schimmel & Co., Reports.*

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I have to acknowledge the kindness of Messrs. Scott, Greenwood & Son for allowing me a liberal use of my work entitled "The Chemistry of Essential Oils and Artificial Perfumes," the copyright of which they own.

ERNEST J. PARRY.

# PERFUMERY

**ABIES OILS.**—The oils usually known as pine needle oils include those obtained from various species of *pinus*, *larix* and *abies*. (See under "Pine Needle Oil.")

**ABSOLUTES.**—The term "absolutes" is applied to the most highly concentrated form of floral perfumes which can be made. There are numerous trade names for these highly-concentrated preparations, but they are, in the main, identical with, or very similar to, the substances known commonly as absolutes. The extraction of the perfume material of the plant by means of a volatile solvent, which is afterwards recovered by distillation, was used, in a more or less experimental manner, about the year 1835. Robiquet appears to be the earliest experimenter in this direction, but it was due to Massignon and to Naudin to make the process a commercial success. During the past thirty years the extraction has been carried out on a commercial scale. The oily, waxy, and resinous matters of the plant are extracted from the plant substance by means of the volatile solvent, leaving behind the bulk of the inert and inodorous matter. The volatile solvent, such as petroleum ether, is recovered by distillation, generally under reduced pressure, in order to keep the temperature as low as possible. The solvent must be able to dissolve the whole of the odorous substances present, and must have no chemical action on them. It should also dissolve as little as possible of any inodorous substances. Further, it should boil at the lowest possible temperature and leave no odour behind when evaporated. The semi-solid residue left behind on the evaporation of the solvent consists of the odorous constituents of the plant, together with the inodorous waxy matter. These substances are usually known as "concrètes." They are either sold as such (when the perfumer has to filter off the matter insoluble in alcohol), or they are further treated and converted into absolutes. This is effected by treating them with alcohol in shaking machines, and the alcohol is filtered. It is then exposed to a very low temperature and dissolved wax is thus separated. The clear alcoholic solution

## PERFUMERY

is now either evaporated at a low temperature and the residue sold as an absolute, or the perfume material is isolated by salting out, when it can be separated, or it can be dissolved out from the alcohol mixed with brine, by petroleum ether, which is then evaporated, and the residue is the absolute.

An absolute is understood to be a pure vegetable product free from the addition of synthetics, and it should form a clear solution with alcohol, which ought not to precipitate on cooling.

The solvent in almost general use to-day is a highly-purified petroleum ether. So far as any comparative figure can be given, it may be said that the concretes are about forty times as strong as the corresponding pomades known as "No. 36," and the absolutes stronger still.

**ACACIA.**—This genus of the natural order *Leguminosæ* includes a number of plants with sweet-scented flowers. The two of really commercial importance are *Acacia Farnesiana*, which yields the cassie perfume, and *Acacia dealbata*, which, with several other species, yields the well-known mimosa perfume.

A small quantity of perfume is obtained for local use in Australia from various species of acacia known commonly as wattle blossoms.

The perfume of the cassie flowers is very delicate, and is best dealt with in the form of a pomade, but it is also made as an absolute flower oil. It is widely distributed over the warmer districts of all continents. For example, it is found in Egypt, Australia, the Hawaiian Islands, the Philippine Islands, North and South America, France, Algeria, Syria, northern India, and New Caledonia. In Europe the collection of flowers commences when the plants are three years old. Each tree yields about 500 to 600 kg. of flowers, which are gathered twice weekly during the months of September, October, and November, and sometimes even in December. A good deal of pomade was at one time made in India, but to-day very little is manufactured there. In Syria, near Bayreuth, the pomade is made, as the cassie tree is there very plentiful. In the south of France the plant flourishes best in the neighbourhood of Grasse and Cannes, where it is known as "cassie ancienne" or "casillier de Farnèse." A less odorous species is *Acacia cavenia*, known as "cassie romane."

The principal flowering season is October-November, whilst in favourable seasons flowers are picked as late as January or February. Essential oil of cassie, a somewhat rare product, has

a specific gravity 1.040 to 1.058; refractive index, 1.5130 to 1.5150; ester value, 114 to 230; and melts at about 18°. It contains farnesol, geraniol, linalol, benzaldehyde, eugenol, benzyl alcohol, methyl salicylate, decylic aldehyde, cuminic aldehyde, anisic aldehyde, *para*-cresol, and a ketone of violet colour.

The essential oil from *Acacia cavenia* contains eugenol, methyl salicylate, benzaldehyde, benzyl alcohol, anisic aldehyde, eugenol methyl ether, and a ketone with a violet odour. Linalol and decylic aldehyde are also probably present.

Cassie, either in the form of a pomade, concrete, or absolute, is of great value in the preparation of violet bouquets. Synthetic cassie perfumes can be, and are, manufactured on the basis of the composition of the essential oil given above, assisted by the judicious use of traces of the higher fatty aldehydes, especially the 12 carbon aldehyde, a small quantity of one or other of the ionone ketones, and *para*-methyl acetophenone.

*Acacia dealbata* (*Mimosa dealbata*) is the principal tree whose flowers are used for the preparation of the mimosa perfume, in the same way as the cassie perfume. The crop is gathered from February to March. *Acacia floribunda* is also used for the perfume. Artificial mimosa resembles artificial cassie, and methyl-acetophenone and its homologues are used in its preparation, together with methyl-heptin-carbonate and hydroxycitronellal.

The oil from *Robinia pseudacacia* is of good odour value, but is scarcely a commercial article. The flowers are sometimes made into a concrete or absolute flower oil, which has a typical acacia odour. The essential oil has a specific gravity 1.05, and contains linalol,  $\alpha$ -terpineol, benzyl alcohol, indol, and heliotropin (Elze, *Chem. Zeit.*, 34, 814).

(For an account of other species, see *Les Parfumes de France*, 1924, 13, 35.)

**ACETEUGENOL.**—This body,  $C_{12}H_{14}O_3$ , is a crystalline compound formed by the action of acetic anhydride on eugenol. It melts at 29°. It is present to a very small extent in oil of cloves.

**ACETIC ACID.**—Solutions of acetic acid are employed in the manufacture of toilet vinegars. It should be pure, water white, and free from the slightest empyreumatic odour. It is an acid obtained by the distillation of wood (also synthetically), and has the formula  $CH_3COOH$ . The following table gives the most useful strengths as determined by the specific gravity, which,

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where a specific gravity over 1.050 is being dealt with, must be checked by titration :—

Sp. gr.	Per cent.	Sp. gr.	Per cent.
1.000 . . .	0	1.065 . . .	55
1.007 . . .	5	1.068 . . .	60
1.014 . . .	10	1.071 . . .	65
1.021 . . .	15	1.073 . . .	70
1.028 . . .	20	1.075 . . .	75
1.035 . . .	25	1.075 . . .	80
1.041 . . .	30	1.074 . . .	85
1.047 . . .	35	1.071 . . .	90
1.052 . . .	40	1.066 . . .	95
1.057 . . .	45	1.055 . . .	100
1.061 . . .	50		

**ACETIN.**—The term acetin is used to include the three acetic esters of glycerin, *mono-*, *di-*, and *tri-* acetin. A mixture of these is used as an adulterant of essential oils, but, being much more soluble in water than the natural esters, may readily be detected by washing two or three times with hot water, and noting any decrease in volume of the oil. The acetins are used to some extent as solvents for essential oils, either alone or in conjunction with alcohol; they are miscible in all proportions with 20 under proof spirit. (*Vide* "Artificial Esters.")

**ACETONAPHTHONE.**—This body,  $\alpha$ -naphthyl-methylketone  $C_{10}H_7.CO.CH_3$ , is prepared by condensing naphthalene and acetyl chloride with the assistance of aluminium chloride. It is best condensed in monochlor-benzene solution (Chopin, French patent 536,257). It has a very useful orange-blossom odour, and is useful in admixture with phenyl-ethyl alcohol and methyl anthranilate in the preparation of artificial neroli oils. It forms crystals melting at  $34^\circ$ , and boils at  $295^\circ$ .

**ACETOPHENONE.**—This ketone,  $C_6H_5.CO.CH_3$ , occurs naturally in oil of ladanum resin, and in the oil of an Australian plant, *Stirlingia latifolia*, of which it forms about 90 per cent.

It has a persistent and powerful odour, which is taken advantage of by perfumers in the preparation of perfumes of the type of new-mown hay, syringa, and the like.

It is prepared artificially by pouring acetyl chloride slowly on to a mixture of benzene and aluminium chloride at a low temperature. Hydrochloric acid is evolved, and the product is left for several hours at ice temperature. It is then washed with water, then with dilute alkali, and rectified *in vacuo*. Its oxime melts at  $59^\circ$ .

Acetophenone is a crystalline substance melting at 19° to 20°, and boiling at 200° to 202°. It has a specific gravity 1·033, and refractive index 1·5355. It is used medicinally under the name "Hypnone."

**ACETYLATION.**—See "Alcohols, Determination of."

**ACHASMA WALANG, OILS OF.**—The essential oils have been extracted separately from the leaves, the stems, and the roots of this member of the *Zingiberaceæ*, *Achasma Walang* Val., or *Amomum Walang* Bl., which in Java goes under the name of *daon walang*.

*Roure-Bertrand Fils (Bulletin, April, 1914, 154)* give the following characters of the oils:—

*Oil of the Leaves (yield, 0·25 per cent.)*

Specific gravity	0·850
Acid value	10·1
Optical rotation	—0° 34'
Saponification value	70
Aldehydes (neutral sulphite method).	97 per cent.

*Oil of the Stems (yield, 0·2 per cent.)*

Specific gravity	0·860
Acid value	26
Optical rotation	—0° 58'
Saponification value	75·6
Saponification value after acetylation	285·6
Aldehydes	96 per cent.

*Oil of the Roots (yield, 0·15 per cent.)*

Specific gravity	0·856
Acid value	18·9
Optical rotation	—0° 30'
Saponification value	70
Saponification value after acetylation	285·6
Aldehydes	96 per cent.

**ACHILLEA MOSCHATA.**—This plant, known as the musk-scented milfoil, is found on the Alps at an elevation of 5,000 to 10,000 feet. On distillation of its flowers and leaves it yields an essential oil which has been used to perfume the Swiss liqueur known as *Iva*. It contains cineol, valeric aldehyde, *lævo*-camphor, palmitic acid, and an oxygenated body termed *ivaol*, of the formula  $C_{24}H_{40}O_2$ . The pure oil has a specific gravity 0·928 to 0·960; optical rotation, —12° to —15°; refractive index, 1·4760; and ester value, 18 to 44.

**ACORUS CALAMUS.**—This plant, commonly known as the sweet flag, is a member of a genus of semi-aquatic plants

belonging to the natural order *Aroidæ*. It must not be confounded with the Indian "calamus aromaticus," which is now recognised as one of the *Andropogon* family. *Acorus calamus* grows best by the banks of rivers and in marshy ground, being plentiful by the rivers in Norfolk. It is now cultivated in damp marshy places in India and Burmah. In warm climates it develops greater fragrance than it does in England. From the lower part of the thick, jointed rhizome the plants send down numerous long, slender roots, but it is from the rhizome itself that the essential oil is distilled.

The dried rhizome is found in commerce as flattened pieces from 4 to 6 inches long and about  $\frac{3}{4}$  inch thick. It is of a yellowish brown or fawn colour externally. In India the rhizome is used in the preparation of an aromatic vinegar. In Europe the rhizome is used in the form of powder as a constituent of toilet and sachet powders, but its use has decreased of late years.

According to Russell (*Jour. Amer. Chem. Soc.*, 1915, 37, 2387), all parts of the plant contain an essential oil, which varies in characters with the portion of the plant from which it is obtained.

The normal essential oil of sweet flag, which is used to some extent as a perfume material, and also as an ingredient in the flavour of gin and some types of beer, is distilled from the rhizomes. Its specific gravity varies from 0.950 to 0.970; optical rotation,  $+9^{\circ}$  to  $+35^{\circ}$ ; refractive index, 1.5000 to 1.5080; and ester value from 5 to 20.

It contains pinene, camphene, camphor, a sesquiterpene termed calamene, a sesquiterpene alcohol, eugenol, heptylic acid, palmitic acid, and asarylic aldehyde.

There is a Japanese calamus oil, distilled from *Calamus spurius*, which differs somewhat from the oil from *C. aromaticus*, but resembles it in general characters.

**AFRICAN COPAIBA OIL.**—See "*Hardwickia Balsams*."

**AGLAIA FLOWERS.**—The flowers of *Aglaia odorata*, known locally as *Lan-hwa* or *Yu-chu-lan*, are used by the Chinese for the purpose of scenting tea.

**AJOWAN SEED OIL.**—Ajowan seed is the fruit of *Ptychotis Ajowan* (*Carum Ajowan*, *Carum copticum*), a plant known as "true bishop's weed." The plant is cultivated in many parts of Egypt, Persia, Afghanistan, and Bengal. It is indigenous to India. The seed yields from 3 to 4 per cent. of essential oil, having a powerful odour of thymol. In addition to its principal



constituent, thymol, the oil contains cymene, pinene, dipentene, and terpinene. The oil is used on a large scale for the preparation of thymol (*q.v.*). In the native bazaars of India the oil is allowed to evaporate spontaneously, and the crude thymol is sold under the name *Ajwain-ka-phul* (Flowers of Ajowan). The odour of the oil is pungently aromatic. The plant is known by the following vernacular names in the East :—

Arabic . . . . .	<i>Kamuné-muluki.</i>
Persian . . . . .	<i>Nankhah and Zinyan.</i>
Hindustani . . . . .	<i>Ajvayan.</i>
Dukhni . . . . .	<i>Ajvan.</i>
Tamil . . . . .	<i>Omam.</i>
Telegu . . . . .	<i>Omamu or Vamamu.</i>
Malaylim . . . . .	<i>Ayamodakam and Homam.</i>
Canarese . . . . .	<i>Voma.</i>
Bengali . . . . .	<i>Ajvain or Ajvan.</i>
Mahratta . . . . .	<i>Vova-sada and Vova.</i>
Gujerati . . . . .	<i>Ajwan.</i>
Burmese . . . . .	<i>Samhum.</i>

Experimental cultivations have been started in the West Indies, but so far they have not yielded commercially successful results.

The essential oil has a specific gravity 0.910 to 0.930 ; optical rotation,  $+1^{\circ}$  to  $+5^{\circ}$  ; and refractive index, 1.4980 to 1.5005. It contains from 45 to 60 per cent. of thymol, and serves as a raw material for the extraction of this important body.

Bodh Raj Sobti and Puran Singh (*P. & E. O. R.*, 1923, 399) state that in the thymol manufactory of the Scindia Chemical Laboratories, Gwalior, they found a large fraction of a dark residual oil which would not crystallise at all—left as it was after the whole of the thymol was crystallised out from the phenol fraction of the ajowan oil which was obtained by shaking the oil with caustic soda solution. It seemed interesting to identify this material, especially when the presence of carvacrol in ajowan oil had yet to be confirmed. (*Vide* Parry, "The Chemistry of Essential Oils," 3rd edition, vol. i., p. 303.)

Large quantities of this fraction of the phenols were available in the thymol refinery. After repeated distillation and refrigeration, these gave sufficient quantities of a non-crystallising phenol distilling over between  $236^{\circ}$  and  $240^{\circ}$  C. at 746 mm. pressure. It had the following physical constants :—

Specific gravity at $29.0^{\circ}$ C. . . . .	0.9712
Optical rotation . . . . .	0
Refractive index at $28^{\circ}$ . . . . .	1.5230

On combustion found	{ C	. 80.10 per cent.
	{ H	. 9.38 „
Theoretical $C_{10}H_{14}O$	{ C	. 80.00 „
	{ H	. 9.33 „

There are a good number of phenols of the formula  $C_{10}H_{14}O$  which have their boiling points near  $235^{\circ}C$ . In order to eliminate some of these, the methyl ether was prepared.

There are four possible isomeric methyl ethers which have their boiling points near  $216^{\circ}C$ ., viz. :—

- (1) Methyl ether of 4-oxy-3-propyl-1-methyl benzene, boiling point  $216^{\circ}$  to  $218^{\circ}C$ .
- (2) Methyl ether of 6-oxy-3-isopropyl-1-methyl benzene, boiling point  $217^{\circ}C$ .
- (3) Methyl ether of 2-oxy-4-isopropyl-1-methyl benzene (carvacrol), boiling point  $216.8^{\circ}C$ .
- (4) Methyl ether of 3-oxy-4-isopropyl-1-methyl benzene (thymol), boiling point  $216.20^{\circ}C$ .

Further, the methyl ether, on oxidation with 5 per cent. potassium permanganate in alkaline solution, gives an oxymethyl-dicarboxylic acid having a definite melting point. It was prepared as follows :—

The methyl ether was suspended in strong sodium carbonate solution and kept ice cold. Five per cent. potassium permanganate solution (the calculated quantity) was added in portions until the colour was slightly permanent. To destroy this, a little alcohol was added. Manganese dioxide was filtered off and washed with hot water. The filtrate was taken down to a small volume on a water bath, and then acidified with hydrochloric acid. The methoxy acid thus obtained was recrystallised from alcohol. Its melting point was  $277^{\circ}C$ .

Methyl ether of 4-oxy-3-propyl-1-methyl benzene and 6-oxy-3-isopropyl-1-methyl benzene give the same oxy-methyl-dicarboxylic acid melting point  $261^{\circ}C$ ; while methyl ethers of 2-oxy-4-isopropyl-1-methyl benzene (carvacrol and 3-oxy-4-isopropyl-1-methyl benzene (thymol) give the same oxymethyl-dicarboxylic acid which melts at  $277^{\circ}C$ . Therefore, the phenol under investigation can be either thymol or carvacrol.

A drop of ferric chloride was added to an alkaline solution of this phenol; it was coloured green, and after some time changed to a dark brown colour. This led the authors to suspect the presence of carvacrol. This was further confirmed by the colour produced by heating it with formaldehyde (Hermann Endermann,

*Jour. Soc. Chem. Ind.*, 1896, 791-792). A little of the substance was dissolved in commercial formalin, the solution evaporated nearly to dryness at a low temperature, and concentrated sulphuric acid added. The solid residue was coloured orange. To be sure of the colour reactions, a little pure thymol and carvacrol were treated under similar conditions. The colour produced by the carvacrol sample was exactly similar to that produced by the fraction under investigation. For further confirmation, the nitroso compound was prepared, the melting point of which was 153° C.

**ALCOHOL.**—Alcohol is the most important substance used by the perfumer. So many of the substances used in perfumery are only soluble in organic solvents, that water is of comparatively little use. The solvent for the perfumer must be very volatile, and must be sufficiently free from odour not to interfere with the perfume value of the ingredients dissolved therein. Prolonged experience has demonstrated the fact that alcohol is the best solvent which meets the general requirements of the perfumer. There are other solvents, such as isopropyl alcohol (*q.v.*), which are of considerable use, but there is no other that will effectively replace ordinary alcohol without *some* disadvantage.

Alcohol, or ethyl alcohol, is a substance which is obtained universally by fermentation processes. It results from the decomposition of sugar by means of the yeast organism, which breaks sugar down into alcohol and various other secondary constituents. For the perfumer it is of the highest importance that the alcohol employed should be as free as possible from such secondary constituents, and have as little odour as possible. In this country the alcohol generally preferred is grain spirit, which is as free from secondary constituents as possible.

Pure or absolute alcohol, that is, alcohol of 100 per cent. strength,  $C_2H_5OH$ , is a colourless volatile liquid of faint, delicate odour, having a specific gravity 0.794 at 15.5°, and boiling at 78° to 79°.

The perfumer rarely uses alcohol of this strength, as, of course, the duty on alcohol in this country is exceedingly high. His aim is, therefore, to use the lowest strength alcohol possible compatible with efficiency in his products. That efficiency demands that the necessary ingredients shall be perfectly soluble, and that the finished product shall be sufficiently volatile. The considerations that arise, then, are: firstly, the determination of the strength of the alcohol to be used; secondly, the tests necessary to detect impurities in the alcohol; and thirdly, as is very fre-

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quently necessary, the estimation of the alcohol in the finished product.

(1) For all practical purposes the perfumer can rely on the specific gravity of the alcohol as a correct measure of its strength. This is true if it be mixed with nothing else but water ; otherwise it is not true, and the presence of foreign substances must be allowed for.

A term frequently used is proof spirit, together with the expression "degrees under or over proof." The term proof spirit had its origin empirically. The excise officers in early days tested alcohol for duty purposes by pouring a given amount on a given weight of gunpowder. If it was below a certain strength, the gunpowder did not ignite on the application of a light ; if above a certain (empirical) strength, it *did* ignite. Hence the terms under or over proof. To-day, proof spirit is legally defined as alcohol of such a strength that, at 51°, 13 volumes shall weigh as much as 12 volumes of water.

Proof spirit has a specific gravity at 15·5° C., 0·9198, and contains 49·28 per cent. of alcohol by weight, or 57·1 per cent. by volume. The expressions under or over proof mean as follows. If a sample of alcohol contains as much alcohol as corresponds with 80 per cent. of proof strength, it is 20° *under* proof. If it contains alcohol corresponding with 120 per cent. of proof strength, it is 20° *over* proof. The following table gives the strength of mixtures of alcohol and water by volume. These figures are from the table in use in the Government laboratory :—

Specific gravity at 60° F. (15·5° C.)	Absolute Alcohol.		Percentage of Proof Spirit.	Specific gravity at 60° F. (15·5° C.)	Absolute Alcohol.		Percentage of Proof Spirit.
	By volume.	By weight.			By volume.	By weight.	
1000	0·00	0·00	0·00	987	9·65	7·76	16·85
999	0·66	0·53	1·16	986	10·51	8·46	18·34
998	1·34	1·07	2·33	985	11·40	9·18	19·87
997	2·02	1·61	3·52	984	12·29	9·91	21·44
996	2·71	2·17	4·73	983	13·20	10·65	23·02
995	3·42	2·73	5·98	982	14·13	11·42	24·66
994	4·14	3·31	7·24	981	15·08	12·20	26·32
993	4·88	3·90	8·51	980	16·04	12·99	27·99
992	5·63	4·51	9·82	979	17·02	13·80	29·70
991	6·40	5·13	11·16	978	18·00	14·61	31·42
990	7·18	5·76	12·53	977	18·99	15·43	33·15
989	7·98	6·41	13·94	976	19·98	16·25	34·87
988	8·80	7·08	15·38	975	20·97	17·08	36·61

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Specific gravity at 60° F. (15·5° C.)	Absolute Alcohol.		Percentage of Proof Spirit.	Specific gravity at 60° F. (15·5° C.)	Absolute Alcohol.		Percentage of Proof Spirit.
	By volume.	By weight.			By volume.	By weight.	
974	21·96	17·90	38·35	928	53·16	45·47	93·09
973	22·94	18·72	40·06	927	53·65	45·94	93·95
972	23·91	19·53	41·77	926	54·14	46·40	94·80
971	24·85	20·34	43·47	925	54·62	46·87	95·65
970	25·83	21·14	45·14	924	55·10	47·33	96·49
969	26·77	21·93	46·77	923	55·58	47·79	97·33
968	27·69	22·71	48·38	922	56·05	48·25	98·16
967	28·69	23·48	49·98	921	56·52	48·71	98·98
966	29·48	24·23	51·53	920	56·99	49·17	99·80
965	30·34	24·97	53·04	91976	57·10	49·28	100·00
964	31·18	25·68	54·51				
963	31·99	26·37	55·93	919	57·46	49·63	100·62
962	32·79	27·06	57·33	918	57·92	50·08	101·43
961	33·56	27·73	58·68	917	58·38	50·53	102·24
960	34·33	28·39	60·03	916	58·83	50·98	103·05
959	35·06	29·03	61·32	915	59·29	51·43	103·84
958	35·79	29·66	62·60	914	59·74	51·88	104·63
957	36·50	30·28	63·85	913	60·19	52·33	105·42
956	37·20	30·90	65·09	912	60·63	52·77	106·20
955	37·89	31·50	66·29	911	61·07	53·21	106·97
954	38·57	32·09	67·48	910	61·51	53·65	107·74
953	39·22	32·67	68·62	909	61·95	54·10	108·52
952	39·87	33·25	69·76	908	62·39	54·54	109·29
951	40·50	33·81	70·87	907	62·83	54·98	110·06
950	41·13	34·37	71·98	906	63·26	55·42	110·82
949	41·74	34·92	73·05	905	63·70	55·87	111·59
948	42·35	35·46	74·12	904	64·13	56·31	112·35
947	42·95	36·00	75·17	903	64·56	56·75	113·10
946	43·54	36·54	76·21	902	64·98	57·18	113·84
945	44·13	37·07	77·24	901	65·41	57·62	114·59
944	44·71	37·60	78·26	900	65·83	58·06	115·33
943	45·28	38·12	79·26	899	66·25	58·50	116·07
942	45·85	38·64	80·26	898	66·67	58·93	116·81
941	46·40	39·15	81·23	897	67·08	59·37	117·54
940	46·95	39·65	82·19	896	67·50	59·80	118·26
939	47·50	40·15	83·15	895	67·92	60·23	118·98
938	48·04	40·65	84·10	894	68·33	60·66	119·70
937	48·57	41·15	85·04	893	68·74	61·09	120·42
936	49·10	41·64	85·97	892	69·14	61·52	121·14
935	49·63	42·13	86·89	891	69·55	61·95	121·85
934	50·15	42·62	87·81	890	69·95	62·38	122·56
933	50·67	43·11	88·71	889	70·35	61·81	123·27
932	51·18	43·59	89·61	888	70·75	63·24	123·97
931	51·68	44·06	90·49	887	71·15	63·67	124·06
930	52·18	44·53	91·36	886	71·55	64·10	125·37
929	52·67	45·00	92·23	885	71·95	64·53	126·07

# P E R F U M E R Y

Specific gravity at 60° F. (15.5° C.)	Absolute Alcohol.		Percentage of Proof Spirit.	Specific gravity at 60° F. (15.5° C.)	Absolute Alcohol.		Percentage of Proof Spirit.
	By volume.	By weight.			By volume.	By weight.	
884	72.34	64.96	126.77	838	88.68	83.99	155.47
883	72.74	65.39	127.46	837	88.99	84.39	156.02
882	73.13	65.81	128.14	836	89.30	84.78	156.56
881	73.52	66.24	128.82	835	89.61	85.17	157.10
880	73.91	66.66	129.50	834	89.91	85.56	157.63
879	74.30	67.09	130.18	833	90.22	85.95	158.16
878	74.68	67.51	130.86	832	90.52	86.34	158.68
877	75.06	67.93	131.53	831	90.82	86.73	159.21
876	75.44	68.35	132.19	830	91.11	87.11	159.73
875	75.82	68.77	132.86	829	91.40	87.50	160.24
874	76.19	69.19	133.53	828	91.69	87.88	160.75
873	76.57	69.62	134.19	827	91.98	88.27	161.26
872	76.94	70.04	134.84	826	92.26	88.65	161.76
871	77.32	70.46	135.50	825	92.55	89.03	162.26
870	77.69	70.88	136.16	824	92.83	89.41	162.75
869	78.06	71.30	136.81	823	93.11	89.79	162.24
868	78.43	71.72	137.46	822	93.38	90.16	163.72
867	78.80	72.14	138.10	821	93.65	90.53	164.20
866	79.17	72.55	138.74	820	93.92	90.90	164.67
865	79.53	72.97	139.38	819	94.19	91.27	165.14
864	79.89	73.39	140.02	818	94.45	91.63	165.60
863	80.25	73.81	140.65	817	94.71	92.00	166.06
862	80.61	74.22	141.28	816	94.97	92.36	166.51
861	80.97	74.64	141.91	815	95.22	92.72	166.96
860	81.32	75.05	142.54	814	95.47	93.08	167.41
859	81.68	75.47	143.16	813	95.72	93.44	167.86
858	82.03	75.88	143.78	812	95.97	93.80	168.28
857	82.38	76.30	144.40	811	96.21	94.15	168.71
856	82.73	76.71	145.01	810	96.45	94.50	169.13
855	83.08	77.12	145.62	809	96.69	94.85	169.55
854	83.42	77.53	146.23	808	96.93	95.20	169.96
853	83.77	77.94	146.83	807	97.16	95.55	170.37
852	84.11	78.35	147.43	806	97.39	95.89	170.77
851	84.44	78.76	148.03	805	97.62	96.23	171.17
850	84.78	79.17	148.62	804	97.84	96.57	171.56
849	85.12	79.58	149.21	803	98.06	96.91	171.95
848	85.46	79.98	149.80	802	98.28	97.25	172.23
847	85.80	80.39	150.39	801	98.49	97.59	172.71
846	86.12	80.79	150.97	800	98.70	97.91	173.07
845	86.44	81.20	151.55	799	98.91	98.24	173.44
844	86.77	81.60	152.12	798	99.12	98.57	173.80
843	87.09	82.00	152.68	797	99.32	98.90	174.16
842	87.42	82.40	153.25	796	99.52	99.22	174.52
841	87.74	82.80	153.81	795	99.72	99.55	174.87
840	88.06	83.20	154.37	794	99.92	99.87	175.21
839	88.37	83.60	154.92	793.59	100.00	100.00	175.35

(2) *Detection of Impurities.*—The impurities in alcohol will depend to a large extent on the source of the saccharine solution by the fermentation of which the alcohol is obtained. In England, grain starch is the principal source of alcohol; in France it is very largely beet sugar; in Germany, potato starch; and in the United States maize is employed to a very large extent. Rice flour is used considerably in Eastern countries. Grain spirit and beet sugar spirit are usually most valued, as they contain less of the objectionable impurities which tend to spoil the odour of perfumes.

The principal impurities to be guarded against, apart from deliberate additions such as appreciable quantities of methyl or isopropyl alcohols, are aldehydes, esters, and the higher alcohols. These bodies, associated in different proportions in alcohols having different origins, are generally described under the name fusel oil. These impurities are largely removed by diluting the alcohol with water, when a certain amount of the impurities are thrown out of solution, and may be separated, the alcohol being then again concentrated by fractional distillation, the first runnings and the tailings being rejected for retreatment, the middle runnings being almost pure alcohol, mixed with a little water. For very special purposes, alcohol (rectified spirit, spirit of wine) may be still further purified by treatment with chemicals such as silver nitrate, to decompose the last traces of aldehyde, and again distilling. Such highly purified alcohol is often known as Cologne spirit, and is suitable for use in the most delicate perfumes.

The following test, originally due to Mulliken and Scudder, will detect as little as 2 per cent. of methyl alcohol in ethyl alcohol. One cubic centimetre of the sample is diluted to 10 c.c. with water, or, if already dilute, to about 10 per cent. strength. A copper wire spiral is made by winding 1 metre of copper wire, about No. 18 gauge, round a glass rod 7 mm. thick, making a coil 30 mm. long, the remaining portion of the wire being used as a handle. The coil is heated to redness in a bunsen flame, and at once immersed in the liquid contained in a test-tube. This is repeated five or six times, the tube being kept in cold water in order to prevent the temperature rising too much. The liquid is filtered into a wide test-tube and boiled very gently. If an odour of acetaldehyde is perceived, the boiling is continued until it has disappeared. The liquid is now cooled, and a drop of a 0.5 per cent. solution of resorcin is added. A portion of the liquid is then carefully floated on to strong sulphuric acid, allowed to stand, and

then gently rotated. If a rose red-ring appears at the contact zone, methyl alcohol is not present to the extent of more than 2 per cent.—a most unlikely quantity for any deliberate adulteration.

Having determined the strength of the alcohol and the absence of methyl alcohol, the following determinations are, if deemed necessary, made :—

(a) *Total Solid Residue*.—If 50 c.c. be evaporated on a water bath, the solid residue should be so slight as to be unweighable.

(b) *Free Acids*.—If a few drops of phenolphthalein be added to 50 c.c. of the alcohol, 0.2 c.c. of decinormal baryta solution should cause a pink colour to develop. A good perfume spirit should contain less than 3 parts per 100,000 (calculated as absolute alcohol) of free acids calculated as acetic acid.

(c) *Total Aldehydes*.—The best process for the determination of the aldehydes is the official process of the French Government. This is carried out as follows. A standard solution of 0.1 gram of aldehyde per litre is made by dissolving 1.386 grams of aldehyde ammonia crystals (= 1 gram of aldehyde) in about 50 c.c. of pure 95 per cent. alcohol. 22.7 c.c. of normal sulphuric acid solution are added, when ammonium sulphate is precipitated. The liquid is made up to 100 c.c. with 95 per cent. alcohol, and another 0.8 c.c. is added to compensate for the precipitated ammonium sulphate. The liquid is left for twelve hours, after being well shaken, and filtered. About 90 c.c. of water are added, and the whole diluted to 1 litre with 50 per cent. alcohol. This is now practically a 50 per cent. alcoholic solution, and when diluted ten times with 50 per cent. alcohol, is a solution containing 0.1 gram of aldehyde per litre, or 1 in 10,000.

A fuchsine-sulphurous acid solution is prepared by mixing 30 c.c. of a 0.1 per cent. solution of fuchsine in 95 per cent. alcohol, 15 c.c. of a solution of sodium bisulphite in water (specific gravity = 1.308), and 30 c.c. of water. The mixture is shaken and allowed to stand for an hour. Fifteen cubic centimetres of 30 per cent. sulphuric acid are then added, and the liquid made up to 250 c.c. with 50 per cent. alcohol.

The sample to be tested is diluted with water to 50 per cent. strength and 10 c.c. of the standard solution is treated with 4 c.c. of the fuchsine-sulphurous acid solution, and the colour developed is matched by adding 4 c.c. of the fuchsine-sulphurous acid solution to sufficient of the diluted sample. From the amount used the quantity of aldehydes is calculated, and should be returned in parts per 100,000 of *absolute* alcohol. Very fine samples contain



less than 1 part, and should not contain more than about 2.5 to 3.5 parts per 100,000 of absolute alcohol.

(d) *Esters*.—The aldehydes are first removed by boiling for an hour with 3 per cent. of metaphenylene diamine under a reflux condenser. The liquid is then distilled, 90 per cent. being collected, and the distillate made up to its original volume. The esters are now determined by saponification in the usual manner, and are returned as parts of ethyl acetate per 100,000 of absolute alcohol. Crude grain spirit may contain 20 to 50 parts per 100,000, but the finest samples will contain only 4 to 10 parts.

(e) *Higher Alcohols*.—There is no exact method of carrying out this determination, but Marquardt's process, modified by Allen and Schridowitz (*Jour. Soc. Chem. Ind.*, 1902, 815), probably gives the best results obtainable. Two hundred cubic centimetres of the alcohol are boiled under a reflux condenser with 0.2 gram of KOH for one hour, and the liquid distilled until 180 c.c. have passed over. Steam is passed through the residue until 300 c.c. are collected. The alcoholic strength should be as near 50 per cent. as possible, either by the addition of pure alcohol or water, if and as necessary. The exact volume is noted, and 100 c.c. taken for the distillation. This is mixed with saturated brine until the specific gravity is 1.100. The liquid is then extracted with three successive quantities of carbon tetrachloride of extreme purity, the separated carbon tetrachloride shaken with a 50 per cent. solution of potassium sulphate, and finally separated and filtered. It is then oxidised by a solution of 5 gr. of potassium bichromate, 2 gr. of sulphuric acid, and 10 c.c. of water on a water bath for eight hours, under an efficient condenser. The liquid is distilled, firstly over a bunsen burner, and then with steam, until about 300 c.c. have been collected. The carbon tetrachloride is separated and washed with water, the washings being added to the aqueous distillate. This is then titrated with decinormal baryta, using phenolphthalein as indicator, after traces of mineral acid have first been neutralised to methyl orange. It is usual to return the higher alcohols calculated as amyl alcohol, so that the acids so found are calculated to valerianic acid. Each cubic centimetre of decinormal alkali is equivalent to 0.0088 gram of amyl alcohol (or 0.0074 gram of butyl alcohol). Calculated to 100,000 parts of absolute alcohol, the best perfumery spirit should contain less than 10 parts, sometimes as low as 3 parts, per 100,000.

Finally, it is often necessary to determine the strength of mixed

perfumes in alcohol when the specific gravity is useless, owing to the presence of essential oils, etc. The following process (Thorpe and Holmes, *Jour. Chem. Soc.*, 1903, 83, 314) may be used. Care should be taken that all measurements, etc., are made at exactly 15.5°. Twenty-five cubic centimetres of the sample are mixed with about 125 c.c. of water, and the whole saturated with salt in a separator. The mixture is extracted twice with from 50 to 80 c.c. of petroleum ether, the mixed petroleum extracts washed twice with brine, and the washings added to the original liquid. The liquid is distilled until all the alcohol has passed over, and the distillate diluted to 100 c.c. and its specific gravity taken. From this the amount of alcohol is found, and multiplied by 4 gives the percentage in the original sample.

(For further details, see E. J. Parry, "Food and Drugs," vol. i., Scott, Greenwood & Co., London.)

**ALCOHOLS.**—The group of bodies known under the generic name "alcohols" play a very important part in the art of perfumery, both from the natural and the synthetic points of view. The alcohols may, for general purposes, be described as bodies containing one or more hydroxyl (OH) groups, which are characterised by their ability by reactions with acids to exchange themselves for acid residues, and so give rise to esters corresponding with salts of mineral acids. They are distinguished from the phenols—bodies belonging entirely to the closed-chain group of compounds—where one or more of the hydrogen atoms of the ring have been substituted by OH groups. The phenols are sharply differentiated from the alcohols by their acid nature, on account of which they readily combine with alkalis to form alkaline phenolates.

Alcohols are termed monohydric, dihydric, etc., according to the number of hydroxyl groups they contain. Thus ordinary "alcohol," or, more properly, ethyl alcohol  $C_2H_5.OH$ , is a monohydric alcohol; ethylene glycol  $C_2H_4(OH)_2$  is a dihydric alcohol; glycerine  $C_3H_5(OH)_3$  is a trihydric alcohol, etc., etc. The monohydric alcohols are the most important of those which are found naturally in perfume materials, and of those which are manufactured artificially. They are sub-divided into three well-marked groups; these are the primary, secondary, and tertiary alcohols.

The primary alcohols are characterised by the hydrogen being linked by bivalent oxygen to a univalent radical. Thus geraniol,  $(C_{10}H_{17})'-O-H$  has the univalent radical  $(C_{10}H_{17})'$  linked to

the hydrogen atom of the hydroxyl group by the bivalent atom of oxygen. The primary alcohols are characterised by being oxidised (generally) with the formation of aldehydes containing the COH group, and thence to acids containing the COOH group. In primary alcohols, therefore, the OH group is attached to a  $\text{—CH}_2\text{—}$  group.

In secondary alcohols the OH group is attached to a bivalent radical thus,  $\text{H.O—CH} \begin{smallmatrix} \text{R'} \\ \text{R} \end{smallmatrix}$ , where R and R' represent other radicals attached to the linking carbon atom. Thus isopropyl alcohol, which may be represented by the formula  $\begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix} \text{>CH—OH}$ , is a secondary alcohol. They are characterised by not yielding aldehydes on oxidation, but ketones containing the  $\text{—CO—}$  group.

Finally, where the hydrogen is linked up to a trivalent radicle, thus,  $\text{H—O—C} \begin{smallmatrix} \text{R} \\ \text{R'} \\ \text{R''} \end{smallmatrix}$ , the alcohol is termed tertiary. These

alcohols yield neither aldehydes nor ketones on oxidation, but are decomposed by the process. Trimethyl carbinol  $\text{H.O.C} \begin{smallmatrix} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \end{smallmatrix}$  is an example of a tertiary alcohol.

The principal alcohols found naturally in essential oils, or manufactured artificially for perfumery purposes, are monohydric and primary. They exist to a considerable extent in the free state, such as geraniol in palmarosa oil, and also in the form of esters, such as geraniol as geranyl tiglate in geranium oil, and linalol as linalyl acetate in bergamot and lavender oils. The more important of these will be found described under their particular name, and methods for their determination will be found under the headings “Alcohols, Determination of,” and “Esters.”

The alcohols soluble in water are not, except possibly in minute traces, to be found in distilled essential oils, as they have, of course, if present, been dissolved out in the distillation waters. The alcohols present in essential oils are either the open-chain alcohols, such as the alcohols usually classed as “fatty alcohols” and those sometimes classified, as a matter of convenience, as the open-chain “terpene” alcohols of which geraniol is the type; or they are the closed-chain alcohols of the typical “aromatic” or “cyclic” series such as benzyl alcohol, or of the closed-chain “terpene” series such as menthol.

Béhal (*Comptes Rendus*, 1919, 168, 945; and *Roure-Bertrand Fils, Bulletin*, April, 1920, 117), has dealt with the isolation of alcohols in a pure condition after physical methods, such as fractional distillation, have achieved all that is possible. He refers to Pasteur's work on the separation of the two alcohols, contained in the amyl alcohol of fermentation, by means of converting them into sulphuric ethers, acids, and barium salts of different solubility. Later, as he points out, the results of the researches of A. Haller (*Comptes Rendus*, 1889, 108, 140; 1890, 110, 580) on the borneols were more general in their scope. They relate to the properties of dibasic organic acids of acting on alcohols to give acid ethereal salts soluble in alkalies, and whose solutions when saponified liberate the original alcohols. The application of this method to terpene alcohols has been the subject of criticisms by Tiemann and Krüger (*Berichte*, 1896, 29, 901). Dodge, in his investigations of oil of citronella, and numerous other chemists have, however, utilised this method. Haller has also recommended it for obtaining pure methyl alcohol by preparing the acid phthalate of methyl by means of phthalic anhydride.

Bouveault has proposed the use of pyruvic acid to identify the alcohols and separate them from a mixture. He converted the esters to which they gave rise into semi-carbazones, whence the alcohols can be regenerated by saponification.

Phenyl isocyanate and diphenyl-carbamyl chloride have since been used to obtain urethanes.

A. Béhal has taken up an old investigation by Liebig and Wöhler, and perfected a method that leads to the formation of allophanates together with urethanes. It consists in causing cyanic acid to react on alcohols. The urethanes, however, are generally only by-products of the reaction.

This method has been applied to the primary, secondary, and tertiary alcohols, whereas none of the preceding methods were available for the last named. The author has likewise obtained good results with terpene alcohols, those of the benzene series, and lastly with the phenols.

The method employed for the preparation of these derivatives is as follows :—

A current of cyanic acid gas is passed into the cooled alcohol. The gas is prepared by the depolymerisation of cyanuric acid. The latter is obtained by Béhal by causing chlorine to act on urea, then precipitating the cyanuric acid with ammoniacal copper sulphate and decomposing the double salt of copper thus formed, ..

by nitric acid. The cyanuric acid is placed in a tube of 12 mm. internal diameter, which is heated to a dark red from front to back. A current of carbonic acid gas is passed slowly through the tube, in front of which is arranged a chamber 30 cm. long. The tube leading the cyanic acid gas into the alcohol has a wide mouth. The alcohol rapidly becomes heated, and then suddenly swells up as a mass of crystals is formed. The crystals, after being cooled, are pounded in a mortar with absolute ether. The whole is then filtered and washed with ether until the ether filtrate no longer leaves a residue on evaporation. The ether thus removes the uncombined alcohol and the urethane, which is always formed to a greater or less extent.

The insoluble residue consists of the allophanate impregnated with cyanuric acid. The allophanate is then dried until the cyanic odour disappears. It is then dissolved in warm absolute alcohol, benzene or acetone, from which it crystallises on cooling. The product is generally pure with the first crystallisation, and further crystallisations are needless.

In the case of solid alcohols, the author operates with an ethereal solution. All the allophanates thus obtained are crystalline, colourless, and inodorous substances. They are very slightly soluble in cold ether and are somewhat more soluble in cold alcohol, though their solubility is still very slight.

In the acyclic series the tertiary allophanates are easily saponified by boiling water. The alcohol is regenerated and urea is formed with liberation of carbonic acid.

The primary and secondary allophanates are saponified with greater difficulty, and in most cases require a boiling aqueous solution of caustic alkali.

By operating on 5 grams of the alcohol or on a quantity of substance containing 5 grams, the alcohol may be easily isolated and identified by the melting point of its allophanate, the alcohol then being regenerated in order to determine its physical constants.

Among the terpene alcohols, linalol behaves abnormally, and Béhal suggests that it is not an alcohol, but an oxide.

The cyclic alcohols, with the exception of terpineol, follow the normal rule.

In the arylalkyl series the author has observed some marked discrepancies in substances containing phenol functions. But if the phenol function is esterified, the reaction becomes normal. In the case of phenol compounds in presence of alcohols, it is easy to eliminate the former by treatment with alkali.

# P E R F U M E R Y

The alcohols with an ethylene hydrocarbon function also give normal allophanates.

Hofmann (*Berichte*, 1871, 4, 268) was the first to give a theory of the formation of the allophanates, and attributed it to the previous formation of a urethane, on which the cyanic acid subsequently acted. Béhal is inclined to think that dicyanic acid is formed, and that this at the moment of its formation reacts on the alcohol present. Before the treatment with cyanic acid, he advises a fractional distillation, which should be carried as far as possible, after preliminary treatments with caustic soda and bisulphite.

The following are the melting points of the allophanates of the undermentioned alcohols :—

Allophanate.	Melting Point.	Allophanate.	Melting Point.
Methyl . . . . .	212°	Trimethylcarbinol . . . . .	190°
Ethyl . . . . .	190°	Amyl. . . . .	152°
Normal butyl . . . . .	149·5° to 150·5°	Benzyl . . . . .	121°
Isobutyl . . . . .	180·5°	Phenylethyl . . . . .	186°
Isoamyl . . . . .	150°	Ethylvanillyl . . . . .	173°
Hexyl . . . . .	165°	Piperonyl . . . . .	176·5°
Isohexyl . . . . .	162°		(decomp.)
Heptyl . . . . .	160°	Secondary phenylethyl. . . . .	181·5°
Octyl . . . . .	157°	Cyclohexylbutanyl . . . . .	148°
Nonyl . . . . .	158°	Cinnamyl . . . . .	185°
Decyl . . . . .	159°	Cyclopentanyl . . . . .	179·5°
Undecyl . . . . .	155·5° to 156°	Cyclohexanyl . . . . .	179°
		Menthyl . . . . .	213°
Dodecyl . . . . .	159·5°	Carvomenthyl . . . . .	192·5°
Allyl . . . . .	165°	Tertiary menthyl . . . . .	187°
Methylethylcarbinol . . . . .	159·5°	Isopulegyl . . . . .	219°
		Phenyl . . . . .	180°

Most alcohols form numerous well-characterised crystalline derivatives, which are useful both for identification purposes and for purifying the alcohols.

Amongst these may be mentioned the acid esters of phthalic acid. (See *Comptes Rendus*, 1889, 108, 1308 ; 1896, 122, 865 ; *Bull. Soc. Chim.*, 1900, 23, 542 ; *Pharm. Zeit.*, 1899, 44, 258 ; *Berichte*, 1910, 43, 1893.) The general method of the formation of these bodies is as follows :—

Fifty grams of the oil (saponified if necessary) containing the free alcohol (or a fraction of the oil rich in the free alcohol) are

mixed with 50 grams of freshly prepared phthalic anhydride and 25 grams of absolutely dry benzene. The mixture is heated to  $110^{\circ}$  to  $120^{\circ}$  for ten hours in a flask under a reflux condenser. The mixture is cooled, an equal volume of water added, and caustic soda solution added until the mass is just alkaline to phenolphthalein. The mixture is extracted several times with ether to remove oil not acted upon, and the filtered alkaline liquid is acidified with concentrated hydrochloric acid. The oily phthalate separates, is washed with water, and dried. To recover the alcohols from the acid phthalates, the latter are saponified with alcoholic potash, the precipitated potassium phthalate filtered off, the ethyl alcohol evaporated off, and the residual insoluble alcohols are washed and dried.

The phenyl-urethanes resulting from the reaction of phenyl isocyanate and the alcohol are also most useful crystalline compounds for identifying the alcohols, as are also the naphthyl-urethanes. In the preparation of these bodies works on organic chemistry should be consulted.

For a suggested method of separating primary, secondary, and tertiary alcohols, see E. Emmett Reid, *Jour. Amer. Chem. Soc.*, 1917, 1249.

M. D.

**ALCOHOLS, DETERMINATION OF, IN ESSENTIAL OILS.**—The principles on which such determinations are made are based on the conversion of the free alcohols into acetates by the action of acetic anhydride and the estimation of the esters formed. When the oil contains both esters and free alcohols, the calculation becomes somewhat complicated, since the alcohols increase in weight on acetylation, whilst the natural esters are unaffected. It should be pointed out that, as in the process of determining the percentage of esters, the results are not strictly accurate chemical determinations, but are based on the assumption that the predominating alcohol is the only substance reacting with acetic anhydride.

The details of the method generally adopted, which should be strictly adhered to, are as follows :—

Ten cubic centimetres of the oil are gently boiled with 20 c.c. acetic anhydride and 2 grams of fused anhydrous sodium acetate, in a 100 c.c. round-bottomed flask fitted with a reflux condenser, for two hours. The contents of the flask are allowed to cool, 100 c.c. of water added, and the mixture gently warmed on a water bath to decompose the excess of acetic anhydride. The mixture

is then transferred to a separator, the aqueous layer rejected, and the oil washed with successive quantities of 50 c.c. each of brine solution containing 1 per cent. of caustic soda and a little phenolphthalein until the washings are free from acidity. The oil is then dried by stirring with a little anhydrous sulphate of soda, and filtered bright through paper.

A suitable quantity of the oil (2 to 6 grams, according to the proportion of esters present) is weighed out and saponified with 40 c.c. of semi-normal alcoholic potash solution as described under the determination of esters. The percentage of total alcohols in the original oil is then calculated from the following formula:—

$$x = \frac{M \times N}{10(W - 0.042N)}$$

where  $x$  is the percentage of total alcohols in the original oil,

$N$  is the number of cubic centimetres of normal alkali used,

$W$  is the weight of acetylated oil taken.

To obtain the percentage of free alcohols, the saponification value of the original oil must be determined, the saponification value of the acetylated oil calculated, and the following formula will then apply:—

$$\text{Percentage of free alcohols} = \frac{(b - a)y}{0.42016(1335.5 - b)}$$

where  $a$  = saponification value of the original oil,

$b$  = „ „ acetylated oil,

$y$  = molecular weight of the alcohol (monatomic).

In some cases, notably linalol and terpeneol, the alcohol is partially decomposed by acetylation in the above described manner. Boulez (*Bull. Soc. Chim.*, iv., 1907, i., 117) has recommended diluting 5 grams of oils containing these alcohols with 25 grams of purified turpentine and boiling the mixture with 40 c.c. of acetic anhydride and 3 to 4 grams of anhydrous sodium acetate. A "blank" experiment to allow for the apparent alcohol value of the turpentine must, of course, be carried out. (See also *Schimmel's Report*, April, 1907.)

Glichitch (*Bull. Soc. Chim.*, iv., 1923, 33, 1284, and *P. & E. O. R.*, 1923, 401) has proposed a method depending on the use of a mixture of absolute formic acid and acetic anhydride. This method is based upon Béhal's discovery, in 1900, that the mixed anhydride of formic and acetic acids reacts in the cold with alcohols to give formates exclusively, while phenols remain unchanged. Béhal obtained complex results with linalol owing



to the fact that he worked at 50° and used an insufficiently low vacuum for the distillation of the product. It is now shown that esterification of linalol is complete in seventy-two hours at 20° to 25°, the conversion into geranyl and terpinyl formates being negligibly small. The presence of acetic acid, acetic anhydride, and formic acid in the acetoformic anhydride does not affect the results, as these compounds form no addition products with terpenes and sesquiterpenes in the absence of mineral acid.

*Preparation of Acetoformic Anhydride.*—One part of absolute formic acid (D 1.22/15°) is added slowly with constant agitation to 2 parts of chlorine-free acetic anhydride (100 per cent.), the temperature being kept below 15°. The mixture is heated during fifteen minutes to 50° and rapidly cooled. It is kept in a bottle with an emery stopper.

*Method of Estimation.*—Ten cubic centimetres of the alcohol to be estimated are added to 15 c.c. of acetoformic anhydride in a 30 c.c. flask closed with an emery stopper. The mixture is well shaken, plunged into a bath of ice water (which need not be renewed), and allowed to remain for seventy-two to ninety-six hours. It is often possible to esterify in seventy-two hours at 20° to 25°. A greater excess of acetoformic anhydride or a longer time than ninety-six hours has no effect, good or bad. A smaller quantity of the reagent is insufficient for pure linalol. The whole is then poured into 50 c.c. of cold water, well agitated, and left for two hours without heating. It is then washed successively with 50 c.c. of water, 50 c.c. of 5 per cent. NaHCO<sub>3</sub> solution, and finally twice with 50 c.c. of water. The esterified oil is dried and saponified as usual, one and a half hours' hydrolysis being given to ensure the complete saponification of traces of terpinyl formate.

The alcohol content of the original oil is calculated from the formula—

$$\frac{n' \times M}{10.(p.n' \times 0.028)}$$

where  $n'$  = cubic centimetres normal KOH used up,

$p$  = grams of oil taken,

$M$  = molecular weight of the alcohol.

Pure linalol prepared by repeated fractionation of rosewood oil was used as a test sample. It was soluble in 14 volumes of 50 per cent. alcohol, and had boiling point 63° to 63.5°/2 mm. or 82.3° to 82.6°/10 mm., D 0.8630/21°,  $n$  1.4605, and optical rota-

tion — 17·30°. The percentage of linalol determined by the above method was :—

					Per cent.
With	24 hours' formylation	.	.		78·40
"	48 "	"	"	.	89·23
"	72 "	"	"	.	99·15
"	96 "	"	"	.	99·31
"	144 "	"	"	.	99·31
"	240 "	"	"	.	99·15

It has been proposed to determine citronellol in the presence of geraniol by means of formylation, instead of by acetylation, on the supposition that heating with formic acid decomposes the geraniol into terpenes and similar compounds, the citronellol alone being esterified.

C. T. Bennett (*P. & E. O. R.*, 1921, 351) has examined this process critically, and finds it to be unreliable.

The estimation of citronellol by heating for one hour on a water bath with twice its volume of formic acid (100 per cent.) was first proposed by Walbaum and Stephan (*Berichte*, 1900, 33, 2,307).

The method was subsequently used by *Messrs. Schimmel & Co.* for the estimation of citronellol in otto of rose (*Schimmel's Reports*, April, 1901, and October, 1904). The results of several determinations by this method were published in the *Perfumery and Essential Oil Record*, 1913, p. 328, and for comparative purposes it was assumed to be a useful factor. The determination of citronellal by the same method has been recommended by *Schimmel & Co.* ("Volatile Oils," vol. i., p. 581). Simmons, however (*P. & E. O. R.*, 1913, p. 297), showed that the process does not give accurate results. Not only does it fail to completely convert geraniol into terpenes, but it gives high results with pure citronellol. These facts were confirmed by subsequent experiments (*P. & E. O. R.*, 1914, p. 51), when it was shown that a pure citronellol estimating 99·7 per cent. by acetylation indicated 119·8 per cent. by the formic acid method.

In order to further test the method by varying the conditions, the following experiments have been conducted in the analytical laboratory of Messrs. Wright, Layman and Umney, Ltd. :—

#### Experiments on pure citronellol.

Heated for one hour on water bath with		
an equal volume of formic acid	.	99·7
Digested for one hour at 20° C.	.	108·7

Indicated percentage  
of citronellol.

	Indicated percentage of citronellol.
Experiments on pure geraniol.	
Heated for one hour on water bath . . .	46.8
Digested for one hour at 20° C. . . . .	82.2
Experiments on equal weights of geraniol and citronellol.	
Heated for one hour on water bath . . .	29.0
Digested for one hour at 20° C. . . . .	68.8
Experiments on citronellal.	
Heated for one hour on water bath . . .	43.8
Heated for two hours on water bath . . .	33.1
Digested for one hour at 20° C. . . . .	76.0
Experiments on equal weights of citronellal and geraniol.	
Heated for one hour on water bath . . .	29.0
Digested for one hour at 20° C. . . . .	68.8
Experiments on Burmese citronella oil.	
Heated for one hour on water bath . . .	34.6
Heated for two hours on water bath . . .	30.3
Digested for one hour at 20° C. . . . .	68.2
Digested for one hour in freezing mixture.	69.2
Citronellal by absorption with 35 per cent. sodium bisulphite solution . . . . .	52

These results show that the formic acid method is unreliable for the determination of either citronellol or citronellal. These conclusions are confirmed by A. St. O. Pfau (*Jour. Prakt. Chem.*, 1921, 102, pp. 276–282), who finds that the method gives inexact results, in part because a portion of the geraniol is converted into the formic ester. With pure citronellol the author's results were irregular and high when 100 per cent. acid was used, and low with a weaker acid. The action of the 100 per cent. acid yields a mixture of products containing unchanged citronellol, a small amount of volatile liquid which is possibly an aliphatic or cyclic terpene, citronellol formate (boiling point, 99° to 100° at 7 mm.), the compound  $C(CH_3)_2OH [CH_2]_3CH(CH_3)CH_2CH_2OCHO$  (boiling point, 129° C. at 5 mm.; specific gravity, 0.9651; optical rotation, 1° 46'; refractive index, 1.4488), and the corresponding diformate (boiling point, 140° to 141° at 7 mm.).

C. T. B.

**ALCOHOLS, HIGHER FATTY.**—The higher fatty alcohols are quite analagous to the higher fatty aldehydes (*q.v.*), but are so expensive and so unsatisfactory, unless absolutely pure, that they are not largely employed in perfumery. The alcohols from 8 to 12 carbon atoms—as they are usually described—have

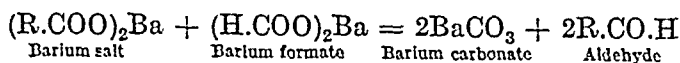
floral odours of a nondescript character, the 12 carbon body recalling the odour of lily of the valley. According to Prins (*P. & E. O. R.*, 1917, 68), octyl alcohol (specific gravity, 0.8278; boiling point, 197°) has a useful rose odour. It also recalls opoponax. Decyl alcohol is useful in preparing flower odours of the rose type. Their employment is confined to rounding off floral odours. An American perfumer has described decyl alcohol as "an alcohol which the up-to-date manufacturer uses to deceive the copier of odours." (See under the respective alcohols.)

**ALCOHOL, ISOPROPYL.**—Isopropyl alcohol or dimethyl carbinol is now being employed to some extent in perfumery, owing to the prohibitive duty on ordinary or ethyl alcohol. Isopropyl alcohol has the formula  $\text{CH}(\text{OH})(\text{CH}_3)_2$ . When pure it is a colourless and nearly odourless liquid of specific gravity 0.786 at 20°, and boiling at 82° to 83°. Its refractive index is 1.3749 at 20°. For perfumery purposes it should be as odourless as possible, otherwise it is quite useless. It is obtained by numerous reactions, such as that between isopropyl iodide and lead hydroxide.

It is sold under various fancy names, and various methods for its preparation industrially have been described. For example, C. Ellis, of New Jersey, describes a method depending on the absorption of the gases from the cracking of petroleum by sulphuric acid of specific gravity 1.8. These gases are very rich in propylene, which combines with sulphuric acid to form an alkyl sulphonic acid which is hydrolysed into the corresponding alcohol. For its comparative harmlessness, *vide* D. H. Grant, *American Journal of the Medical Sciences*, August, 1923.

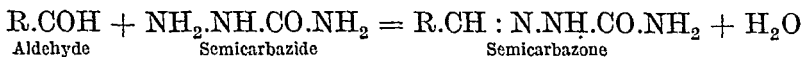
**ALDEHYDES.**—The aldehydes form one of the most important groups of the constituents of essential oils, and also of the more generally employed artificial perfumes. The aldehydes are characterised by containing a  $\text{—CO—}$  group which is combined with one alkyl radical and one hydrogen atom, thus,  $\text{R'—CO—H}$ , ethyl aldehyde, for example, being  $\text{CH}_3\text{—CO—H}$ . If the  $\text{—CO—}$  group is attached to two alkyl radicals, the body is not an aldehyde, but a ketone, thus, acetone  $\text{CH}_3\text{—CO—CH}_3$ .

Aldehydes, in general, may be produced by the oxidation of primary alcohols (*vide* "Alcohols"), or by the distillation of the barium or calcium salt of the corresponding fatty acid with barium formate, thus:—



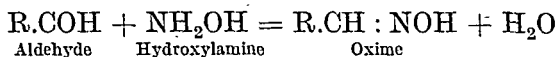
It is often necessary to characterise aldehydes for the purposes of identification. The following are the most important of their crystalline compounds, which can be prepared and their melting points determined for the purpose.

(a) *Semicarbazones*.—Most aldehydes form a crystalline compound with semicarbazide; the condensation products are known as semicarbazones, and are usually crystalline bodies of sharp melting point. They are formed according to the following reaction:—



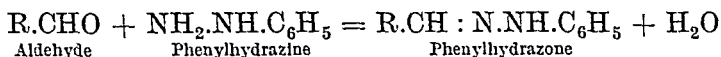
They are obtained by dissolving the aldehyde in alcohol, adding excess of a mixture in equimolecular proportions of semicarbazide hydrochloride and acetate of sodium. The mixture is allowed to stand for several hours, and water is then added. The precipitated semicarbazones are recrystallised from methyl alcohol.

(b) *Oximes*.—Nearly all aldehydes form crystalline oximes by combination with hydroxylamine according to the reaction—



Equimolecular quantities of the aldehyde and hydroxylamine hydrochloride are dissolved in alcohol, and sufficient alcoholic solution of potash added to liberate the hydroxylamine. The whole is heated on the water bath for sixty minutes.

(c) *Phenylhydrazones*.—Most aldehydes combine with phenylhydrazine to form phenylhydrazones, most of which are crystalline. They are formed according to the equation—



They are prepared by heating the aldehyde in alcohol, under a reflux condenser, with phenylhydrazine hydrochloride and sodium acetate for an hour.

Other compounds will be referred to where necessary under particular aldehydes. (*Vide* "Aldehydes, Determination of," and "Aldehydes, Higher Fatty.")

**ALDEHYDES, DETERMINATION OF.**—The determination of aldehydes is one of the operations which the analyst has to undertake most frequently to decide upon the value of raw materials for the perfumer. In such oils as lemongrass, cassia, cinnamon, and lemon the estimation of the aldehydes is the determining factor as to the value of the oil.

The most general process in use amongst analysts depends on

the fact that most aldehydes possess the power of forming compounds with sodium bisulphite or sodium sulphite which are soluble in water. In general, the processes used for the determination of aldehydes depending upon this fact are equally applicable to the determination of ketones. The following processes are of general application to most of the aldehydes and ketones :—

(a) *Bisulphite of Sodium Process*.—Five cubic centimetres of the oil in which the aldehydes are to be determined are placed in a flask holding about 150 to 200 c.c., with a long neck which is graduated in  $\frac{1}{10}$  c.c. To this is added 50 c.c. of a hot 30 per cent. solution of sodium bisulphite, and the whole well shaken. The flask is placed in a boiling water bath and is repeatedly shaken, with the gradual addition of more bisulphite solution, until all crystals formed have disappeared and a clear oily liquid rises to the surface. The shaking should be repeated and vigorous, and the process should last from an hour (lemongrass oil) to two hours (cassia oil). More bisulphite solution should be poured in, up to nearly the top of the neck, and the flask stood aside for twenty-four hours to allow the whole of the unabsorbed portion to rise into the graduated neck. As the specific gravity of both the absorbed and unabsorbed constituents do not differ greatly, the calculation by volume is in practice accepted as accurate. So that if 4 c.c. have been absorbed by the bisulphite and 1 c.c. rises into the neck of the flask, the oil is returned as containing 80 per cent. of aldehydes.

(b) *Neutral Sulphite Process*.—The determination is carried out exactly as in the case of the bisulphite process, except that the absorbing solution is one of neutral sodium sulphite and the end of the process is controlled by a definite reaction. A few drops of phenolphthalein solution in alcohol are added to the contents of the flask, and a red colour is soon developed in the flask due to the liberation of free alkali during the process. A few drops of a 10 per cent. solution of acetic acid are added till the colour disappears, and the shaking repeated. This is done so long as the red colour develops, and when no return of the colour occurs after ten minutes the absorption is complete, and the result is read off in the neck of the flask after twenty-four hours.

(c) *Hydroxylamine Method*.—The fact that aldehydes form compounds with hydroxylamine was first utilised by Walther (*Pharm. Central.*, 1899, 40, 621) for the quantitative determination of this group of bodies. The original process, slightly modified by A. H. Bennett, is practically universally used for the determination of citral in lemon oil and similar oils where only small quantities of

aldehydes are present. Twenty cubic centimetres of the oil are mixed with 20 c.c. of seminormal hydroxylamine hydrochloride solution (in 80 per cent. alcohol), and 8 c.c. of normal alcoholic potash solution and 20 c.c. of 90 per cent. alcohol are added. The mixture is gently boiled for thirty to forty-five minutes under a reflux condenser, and then allowed to cool. The condenser is washed down with water, and the contents of the flask brought up to about 250 c.c. with water. A blank experiment is carried out without the oil. A few drops of phenolphthalein are added and the mixture neutralised to this indicator with alcoholic potash solution. Methyl orange is then added and the mixture exactly neutralised to this indicator with seminormal sulphuric acid. The end reaction is not easy to determine, so that the method of spotting on a white tile with drops of the indicator is resorted to. Each cubic centimetre of seminormal acid is equivalent to 0.076 gram of citral (or the equivalent quantity of any other aldehyde), so that 20 c.c. of the oil (calculated to weight by multiplying by the specific gravity) contains  $0.076 \times x$  grams of citral, where  $x$  is the number of cubic centimetres of seminormal acid consumed.

Further methods of special application will be found under "Citral." (*Vide* also E. J. Parry, "Chemistry of Essential Oils, etc.," vol. ii., Scott, Greenwood & Co., London; and Bennett and Bateman, *P. & E. O. R.*, 1923, 268.)

**ALDEHYDES, HIGHER FATTY.**—During the past few years a most valuable addition to the perfumer's art has been made by the manufacture on a commercial scale of the higher aldehydes of the so-called fatty series: As a group these bodies possess an extraordinarily powerful odour, of a fruity nature, which is so powerful and persistent that a single drop spilt on one's clothes renders one sufficiently odoriferous to be objectionable. They must be used with great discretion and in minute quantities, as otherwise the great improvement effected in a floral odour by their use tends to pass to an objectionable and penetrating strength which spoils the whole bouquet. Properly blended and used with discretion, they are of the highest value to a perfumer who wishes to "create" his own proprietary bouquets. They are equally of value in the rounding off of fruit essences. The following are the principal of these peculiar aldehydes, which, on account of their proneness to oxidise, are frequently sold in 10 per cent. alcoholic dilutions, which are very convenient for use in measuring out very minute quantities.

*Heptylic Aldehyde*,  $\text{CH}_3(\text{CH}_2)_5\text{CHO}$ .—This body is also known as *cenanthylic aldehyde*, and is prepared by the dry distillation of castor oil under a pressure of 100 mm. Only small quantities can be dealt with at a time. It may also be prepared by “esterifying” castor oil by methyl alcohol, using hydrochloric acid as the condensing agent and distilling *in vacuo*. When the temperature rises to  $250^\circ$  at 12 mm., no more is distilled, as the residue is more or less unaltered castor oil. The aldehyde is accompanied by methyl undecylenate, and can be separated by means of its bisulphite compound. It is an oil of strong fruity odour, boiling at about  $152^\circ$ , and having a specific gravity 0.820 and refractive index 1.4150.

*Octylic Aldehyde*,  $\text{CH}_3(\text{CH}_2)_6\text{CHO}$ .—This is the eight carbon aldehyde, and is found naturally in neroli and rose oils. It is of considerable value in perfumes of the rose, jasmin, geranium, neroli and orange types. The starting point of this body is cocoa-nut fat. The fat is saponified, and the fatty acids separated by the addition of dilute sulphuric acid. The aqueous liquid is extracted with petroleum ether, to obtain the fatty acids soluble in water, and these are added to the previously separated fatty acids. The principal fatty acids present are caprylic and lauric acids. These are now washed with a little water, dried over anhydrous sodium sulphate, and heated under a reflux condenser for six to eight hours with their own weight of methyl alcohol and a small amount of sulphuric acid. Water is then added, and the oil separating is washed with water and then with dilute alkali. The esters so formed are then fractionated *in vacuo*; the earlier runnings containing most of the methyl caprylate, whilst the later runnings contain the methyl laurate.

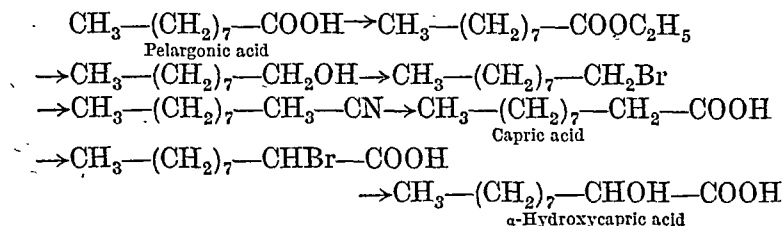
The methyl caprylate is reduced by sodium and alcohol, and yields octyl alcohol  $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$ . This body is then converted by a controlled oxidation into octylic aldehyde. It is a liquid of powerful fruity odour, having a specific gravity 0.827, refractive index 1.4195, and boiling point  $82^\circ$  at 13 mm., or  $175^\circ$  at 760 mm.

*Nonylic Aldehyde*,  $\text{CH}_3(\text{CH}_2)_7\text{CHO}$ , is the nine carbon aldehyde of the series, and occurs naturally in both rose and orange oils. It is used in the same manner as octylic aldehyde. It is an oil of specific gravity 0.8277, refractive index 1.4245, and boiling point  $92^\circ$  at 13 mm. Its melting point is from  $+5^\circ$  to  $+7^\circ$ . It is prepared as follows: Undecylenic acid, one of the products of the dry distillation of castor oil, is carefully melted with caustic



potash and water until no more hydrogen is given off. The mass is exhausted with water, and dilute sulphuric acid is added to the aqueous extract. This precipitates pelargonic acid, which is esterified with ethyl alcohol in the usual manner. The ethyl ester is reduced by sodium and alcohol to nonylic alcohol, which, by controlled oxidation, yields nonylic aldehyde. (*Vide* also Lewinsohn, *P. & E. O. R.*, 1924, 12.)

P. Bagard (*Bull. Soc. Chim.* (4), 1, 346) has prepared nonylic aldehyde by the dry distillation of  $\alpha$ -hydroxycapric acid, which he obtains by starting from pelargonic acid and passing through the intermediate stage of capric acid by means of the reactions—



The same author has obtained decylic aldehyde by the distillation of  $\alpha$ -hydroxyundecylic acid prepared from undecylic acid, which is itself obtained from undecylenic acid.

The characteristic derivatives of these aldehydes described by Bagard (for their preparation, see the original paper) are: the semicarbazone of nonylic aldehyde, melting point  $100^\circ\text{C}$ .; the oxime of nonylic aldehyde, melting point  $64^\circ\text{C}$ .; the oxime of decylic aldehyde, melting point  $69^\circ\text{C}$ .; the azine of decylic aldehyde, melting point  $34^\circ\text{C}$ . (*Roure-Bertrand Fils, Bulletin*, May, 1908, 44.)

*Decylic Aldehyde*,  $\text{CH}_3(\text{CH}_2)_8\text{CHO}$ , or the ten carbon aldehyde of the series, is prepared in the same manner as nonylic aldehyde, starting from capric acid instead of pelargonic acid. It is most useful in the reproduction of the odours of violet, orris, neroli, cassie flowers, rose and orange. It is probably the most generally used of the series so far as perfumers are concerned. It is an oil, boiling at about  $212^\circ$ , of specific gravity about 0.828 to 0.834, and refractive index 1.4298. (See above, under "*Nonylic Aldehyde*.")

*Undecylic Aldehyde*,  $\text{CH}_3(\text{CH}_2)_9\text{CHO}$ , is the eleven carbon aldehyde of the series. This aldehyde is made from the methyl ester prepared from the crude lauric acid of cocoanut fat, as described under "*Octylic Aldehyde*" above. The methyl laurate is saponified in the usual manner, and the resulting lauric acid is

degraded according to the method of Blaise. It is treated with  $\text{PCl}_5$ , which transforms it into lauryl chloride, which is brominated and the resulting compound hydrolysed to bromo-lauric acid. This is converted into oxylauric acid by means of caustic alkali. Oxylauric acid is directly converted into undecylic aldehyde by heat. This aldehyde, which has an intense floral and fruity odour, boils at  $117^\circ$  to  $118^\circ$  at 18 mm. It has a specific gravity 0.825 at  $23^\circ$ , and refractive index 1.4320.

*Duodecylic Aldehyde*,  $\text{CH}_3(\text{CH}_2)_{10}\text{CHO}$ , or laurinic aldehyde, was originally recommended for blending with violet perfumes, but is not well adapted to this purpose. It results from the reduction of ethyl laurate by sodium and alcohol, and controls oxidation of the resulting alcohol. It is a solid body, melting at  $44^\circ$  to  $45^\circ$ , boiling at  $185^\circ$  at 100 mm., and rapidly oxidising to lauric acid. It should therefore be kept in alcoholic solution.

*Tridecyl Aldehyde*,  $\text{CH}_3(\text{CH}_2)_{11}\text{CHO}$ .—This aldehyde has no distinctive flower perfume, but is exceedingly powerful, and can be used in most floral perfumes. American perfumers state that it has been used with great success by those wishing to create special bouquets.

Tetradecyl and hexadecyl aldehydes, containing 14 and 16 atoms of carbon respectively, have intense odours, the former recalling peach, and the latter strawberry. Used in extremely minute quantities they are of great value to the perfumer, but if the quantity exceeds mere traces the composition is ruined.

*Hexylenic Aldehyde*,  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}:\text{CH}\text{CHO}$ , is an unsaturated aldehyde of the fatty series. It has an odour recalling those of vine and strawberry leaves.

(Refer to Weyl, "Méthodes de chimie organique"; and to Ullmann, "Enzyklopedie d. tech. chemie," vol. 9.)

A. G.

**ALECTORIA.**—This is one of the lichens growing on oak and other trees from which the extract known as mousse de chêne or oak moss is manufactured. The perfume obtained is not so fine as that from other lichens such as *Evernia* species.

**ALLSPICE.**—Allspice or pimento consists of the dried unripe fruits of *Eugenia pimenta* (*Pimenta officinalis*, Lindley), a plant belonging to the natural order *Myrtaceæ*. The spice takes its name from its resemblance in perfume and flavour to a mixture of cinnamon, cloves, and nutmeg. It is sometimes known as Jamaica pepper.

The plant is a native of the West Indies, found on calcareous

soils near the coast in Cuba, Hayti, Trinidad, Domingo, and various islands of the Caribbean Sea. The chief part of the world's supply, however, comes from Jamaica. Mexico, Costa Rica, and Venezuela also produce some of the spice. The fruit, after gathering, is carried in baskets to the barbecue, a paved court divided into compartments by a low sill so that the berries of different days' gathering may be kept separate. They are spread out in the sun and turned over with a wooden rake so as to expose them thoroughly to the sun. They take from three to twelve days to dry, and must be well protected from damp, which damages them materially. The average annual output from Jamaica is about 11,000,000 lb. (*Vide* Ridley, "Spices," Macmillan & Co., London.)

The berries yield from 3 to 4.5 per cent. of essential oil on distillation, which contains a large proportion of eugenol. It has the following characters: specific gravity, 1.024 to 1.056; optical rotation,  $-0^{\circ} 40'$  to  $-5^{\circ}$ ; refractive index, 1.5250 to 1.5350; and eugenol value, 65 to 80 per cent. It is soluble in twice its volume of 70 per cent. alcohol, with, at most, slight turbidity.

The oil distilled from the pimento leaves is also rich in eugenol. Experiments on a considerable scale are being carried out by the Department of Agriculture of Jamaica with a view to marketing the oil for the extraction of its eugenol for vanillin manufacture. The leaves yield from 0.4 to 1.2 per cent. of oil, usually containing from 85 to 92 per cent. of eugenol, although the leaves from the Walderston district often yield oils of much lower eugenol value. The departmental chemist, Mr. E. E. A. Campbell, considers that distillation by means of dry steam under pressure is the best method to be adopted, and he does not consider that the addition of salt to the water in the stills is of any special value.

**ALLYL - PULEGONE.**—Haller and Ramart (*Comptes Rendus*, 1924, 179, 120) have prepared a number of alkyl-pulegones from the pulegone obtained from American pennyroyal oil. They describe it as having an odour resembling those of ionone and oil of vetivert, and consider that it may have a commercial value.

**ALLYL SALICYLATE.**—This compound,  $\text{CH}_3\text{CH:CH.OOC(OH).C}_6\text{H}_4$ , is prepared by heating under a reflux condenser a mixture of equal parts of salicylic acid and allyl alcohol with a little sulphuric acid. It is a liquid of floral and fruity odour, boiling at  $247^{\circ}$ . It is not used much in perfumery, but has been

recommended for modifying flower odours (*Rev. Chem. Ind.*, 1911, p. 129).

**ALMONDS, OIL OF.**—An essential oil is obtained from the kernel of the bitter almond, *Prunus amygdalus*, which is identical with that obtained from either peach or apricot kernels. These oils are so nearly identical that for all practical purposes they are interchangeable.

Bitter almond oil does not exist as such in the kernels, but results from the action of water on a glucoside, amygdalin, which is present, under the influence of the ferment, emulsin, which is also present. In commerce the fixed oil is expressed, and the press cakes are ground up and soaked for twenty-four hours in water usually containing some salt. The essential oil is by this time fully developed, and is then distilled. The glucoside on decomposition yields dextrose, benzaldehyde, and hydrocyanic acid. The essential oil consists almost entirely of benzaldehyde, with several per cent. of the highly poisonous hydrocyanic acid. This is removed in various ways; for example, by mixing the oil with water, red oxide of mercury, slaked lime, and ferrous chloride, out of contact with the air, and heating it on a water bath. The hydrocyanic acid is decomposed, and the rectified oil now consists of nearly pure benzaldehyde.

As hydrocyanic acid is a very deadly poison, it is of the highest importance to see that it is free from any traces of the acid. Such oil is sold as "S.A.P." (*sine acid. prussic.*). In order to test for this, a few drops are dissolved in alcohol and a few drops of solutions of ferric chloride and ferrous sulphate are added. A slight excess of caustic soda solution is then added, and the precipitate formed is dissolved in pure hydrochloric acid. A deep blue colour or precipitate (prussian blue) appears if traces of hydrocyanic (prussic) acid are present.

A pure bitter almond oil free from prussic acid has a specific gravity 1.049 to 1.055, refractive index 1.5420 to 1.5460, and boiling point 179°.

The oil requires careful preservation away from air and light, especially if it contains traces of water. It is liable to oxidise rapidly if not so preserved, with the formation of benzoic acid.

This is determined by titration with  $\frac{N}{2}$  caustic alkali, and should not, in good samples, exceed 1 per cent.

The old adulteration of almond oil with nitrobenzene is now quite apocryphal, the only adulterant used in actual practice

being artificial benzaldehyde (*q.v.*). If the latter body contains more than the merest trace of chlorine (which is introduced during the process of manufacture), it is not suitable for perfumery purposes, since it tends to darken any pale substance, such as white soap, which it has been added to. But if the artificial benzaldehyde be absolutely pure, it forms an excellent substitute for the natural oil, at a very much lower price.

It is usual to say that the natural oil is a trifle more delicate in odour, but this is very doubtful, and as a large proportion of the oil sold as natural is, in fact, almost, if not quite, entirely artificial, the perfumer is recommended to pay attention to the artificial benzaldehyde or to purchase the natural oil from recognised actual distillers of repute. (*Vide* "Benzaldehyde.")

**ALOE WOOD.**—*Vide* "Linaloe oil."

**ALOYSIA CITRIODORA.**—*Vide* "Verbena Oil."

**ALPINIA OILS.**—The fresh roots of *Alpinia Malaccensis* yield about 0.25 per cent. of essential oil containing methyl cinnamate. It has a specific gravity 1.039 to 1.047 at 27°; optical rotation, + 0° 15' to + 1° 30'; refractive index, 1.5477; and saponification value, 256 to 278.5. The leaves, according to van Romburgh (*Kon. Akad. Wetén. Amsterdam*, 1898, 550), yield 0.16 per cent. of essential oil containing pinene, and 75 per cent. of methyl cinnamate. Its specific gravity is 1.020 at 26°, and optical rotation + 6° 5'. Ultée (*Annalen*, 1914, 405, 175) examined the oil from *Alpinia Galanga* and found it to contain 50 per cent. of methyl cinnamate and 20 to 30 per cent. of cineol. The oil had a specific gravity 0.974 to 0.985; optical rotation, + 4° to + 6°; and refractive index, 1.5164. Gardies (*La Parfumerie Moderne*, 1923, 109) has reported on an oil from Tonkin, known as *Beu-Rieng*, which possesses a fine odour of an infusion of tea. It is possibly an *Alpinia* oil. It has a specific gravity 0.902; optical rotation, + 8° 8'; refractive index, 1.4884; esters, 3.8 per cent.; and free alcohols, 33.8 per cent.

**AMBER, ARTIFICIAL.**—The so-called artificial ambers or "ambres" are merely mixtures of heavy odour-bearing substances together with (usually) animal fixatives. For example, musk, civet, castor, mousse de chêne, balsams of Peru and Tolu, storax and cinnamic esters enter into their composition. The odour is generally far more pronounced than that of ambergris. A nitrated dibromo-butyl-*m*-cresol methyl ether, melting at about 100°, has been suggested as an artificial amber.

**AMBERGRIS.**—Ambergris is an exceedingly valuable raw material of perfumery, as are several other animal products ; it is also very expensive. It is an opaque grey, yellowish, or black material, occurring in lumps of all sizes, the largest piece yet recorded being one weighing about 200 lb. It is found on the sea coast or floating on the sea near the coasts of India, Africa, and Brazil. About thirty years ago a large proportion of the ambergris sold on the London market was collected by the whalers of Tasmania and New Zealand who plied their trade in the Antarctic Ocean. The industry has now ceased to exist so far as Tasmania is concerned, but the New Zealand fishermen occasionally bring in some ambergris. As this substance has been surrounded by mystery for many years, it will be of interest to briefly note the following views which early writers have expressed as to the actual origin of ambergris. An early writer, named Klobius ("Perfumery" (E. J. Parry), Sir Isaac Pitman & Sons, Ltd., p. 73), gives, amongst others, the following views which have been entertained as to its origin :—

(1) It was believed to be the excrement of a bird, common in Madagascar, melted by the sun's heat, washed out to sea, swallowed by a whale, and passed through its body unaltered. (2) Others believed it to be excrementary material of certain cetaceous animals. (3) It was surmised to be a wax or gum exuding from certain trees growing on the sea shore, which dropped into the sea, congealed, and so became ambergris. (4) A common idea in the Orient was that it sprang from the bed of the sea as naphtha does from the earth, or that it was a kind of bitumen gradually working up from the ocean and hardening in the sun. (5) By some it was held to be a kind of marine fungus torn up from the bottom of the sea by violent tempests. (6) The origin of ambergris was also ascribed to honeycombs which had fallen into the sea from rocks where bees had built their nests. (7) Dr. Boylston and Mr. Dudley (*Phil. Trans.*, 385, 387) asserted that ambergris was an animal concretion found in balls in the body of the male sperm whale. (8) A certain Herr Neumann, chemist to the King of Prussia (*Phil. Trans.*, 433, 434, 435), denied that ambergris was an animal product at all, and that, if it were found in whales, it must have been first swallowed by them. His own opinion was that it was a species of bitumen exuding from the earth into the sea. An old scientific work of the eighteenth century states : "The pieces are frequently seen composed of divers strata . . . with stones and other bodies enclosed within.

and the strata are sometimes full of little shells . . . whence it may be conjectured that the ambergris had originally been in a fluid state . . . and enveloped such bodies as happened to be in its way."

Ambergris is now definitely known to be a pathological secretion of the sperm whale *Physeter macrocephalus*. Sometimes the whale manages to reject the secreted ambergris, and then recovers from his disease; otherwise he dies. As a rule, the dead body is eaten by fish and the ambergris liberated, when it may be found floating on the water or may be washed ashore. If a sick whale is caught alive, the whalers may make more out of the ambergris than out of the whole carcass.

Jean Gattefossé, in an article on ambergris (*La Parfumerie Moderne*, 1920, 259), gives the following as the method by which ambergris is secreted by the sperm whale. The odorous constituents of ambergris, in his opinion, exist already formed in certain cephalopods such as *Eledone moschata*, upon which the whale preys to a very considerable extent. In normal circumstances these substances, as well as the crystalline ambrein, are expelled in the fæces. But if the whale be suffering from a certain micro-organic intestinal disease, these bodies are not expelled. The lumps of ambergris are then formed by the crystallisation of the ambrein with other matter, as those substances not concerned in the formation of the calculi are consumed by the bacteria. The lumps are then expelled fortuitously or, if not, result in the animal's death.

According to V. Hasslauer (*La Parfumerie Moderne*, 1921, 56), ambergris is a calculus formed in the sperm whale by the undigested residues of its food, combined with biliary and gastric juices, blood, and sometimes fæcal matter. The calculus, when found in the interior of the animal, is not of the same quality as that which is expelled. The sperm whale is very migratory, going far afield in search of his food. It furnishes ambergris varying in character according to where it is caught, thus indicating that the nature of the food influences the character of the ambergris. Hasslauer claims that it is possible, from the odour and aspect of the ambergris, for an expert to say from what part of the world it comes. Ambergris which has been expelled and exposed to the sun for several years is certainly of the finest quality.

Some excellent work on the formation of ambergris was commenced by Bauregard ("Les cryptogames de l'ambre gris," *Ann. de micrographie de Miquel*, 1898). He separated an organism,

which he called *Spirillus recti Physeteris*, from the intestines of the animal which appears to be responsible for slowly attacking the faecal matter and thus contributing to the formation of the calculus. His regretted death stopped this very promising investigation.

The value of ambergris in perfumery lies in its very high fixative power, coupled with a slight animal odour, which has always been an attraction in the most refined perfumes so long as it is not too highly accentuated. In common with other animal perfumes, it has in some quarters held a reputation as an aphrodisiac, but this is quite without foundation.

It occurs in characteristic lumps of grey to greyish-yellow or black colour, with a characteristic odour and a somewhat greasy surface. It has a specific gravity of about 0.900 to 0.920 and softens at about 30°, melting at about 40°.

The exact composition of ambergris is not known. Pelletier and Caventou ("Traité de chimie," 1805) claimed to have isolated a substance which they term ambrein from it, and Chevalier, in 1828, again separated it. In 1912 Riban found that this was a mixture, but by repeated recrystallisations he isolated a pure body, for which he retained the name ambrein, and which melts at 82°. Traces of aromatic acids and of an essential oil are also present. The actual odour bearer has not yet been definitely characterised.

Ambergris is used in perfumery in the form of an infusion in 90 per cent. alcohol, usually of about 5 per cent. strength. It is usual to macerate with regular shaking for a period of from one to three months.

Artificial ambergris and similar preparations have no relationship with the natural substance, but are merely "imitation" ambergris, having an entirely different odour, but which are useful as fixers and contribute to the "heavy" type of odour.

The *P. & E. O. R.* (1922, 300) gives the following details of the examination of true and false ambergris by H. I. Cole, of the Bureau of Science, Manila :—

In 1912 Riban (*Comptes Rendus*, 1912, 154, 1729–1732; *Bull. Soc. Chem.*, 1912, iv., 11, 754–757) investigated ambrein more closely. He had come into possession of a small quantity of ambrein which had, in the course of time, separated out from the alcoholic liquid in a bottle containing extract of ambergris. The substance, after being recrystallised from alcohol, melted at between 82° and 86° C. It is a white crystalline solid separating from its alcoholic solution in slender needles. Combustion showed



it to possess the formula  $C_{23}H_{40}O$ . The compound tends to remain in the superfused state when melted, even if sown with crystals. When warm and dry, it becomes highly electrified on slight rubbing. It is not optically active, has a neutral reaction, and is insoluble in water, but soluble in most organic solvents. When acted on by bromine in carbon tetrachloride solution, it gives an octo-bromo derivative  $C_{23}H_{32}OBr_8$ , a white vitreous solid. Chlorine, under similar conditions, decomposes it. On warming ambrein with phosphorus pentachloride, a white amorphous mass of pentachloro ambrein  $C_{23}H_{35}Cl_5O$  is obtained.

The physical constants of ambergris as given in literature vary widely. No chemical methods for its identification are to be found in the literature available. The Chinese test its purity by scraping it upon boiling tea, in which they consider it should dissolve.

A number of substances suspected of being ambergris have been submitted to the Bureau of Science for identification, but one in particular is so generally considered to be the genuine article as to deserve the name "supposed ambergris." This substance is usually found floating far out at sea in localities known to have yielded ambergris. It is picked up by fishermen and sold to the Chinese and Moros as ambergris. It has been shipped through the Custom House of Manila to Japan, rated as "ambergris," and is used by the natives for medicinal purposes, and by the Chinese and Moros probably as an aphrodisiac. In all physical appearances it closely resembles ambergris. It occurs in the same places, is found in the same quantities, and has approximately the same specific gravity, and a similar mottled appearance. It, however, has a slightly different odour, and becomes brittle on ageing, while true ambergris apparently does not. Since no methods of identifying it positively as ambergris were available, the matter was referred to the Bureau of Chemistry at Washington. That bureau reported that "there are no satisfactory methods by which it is possible to identify ambergris. Perfumers are in a better position to determine the genuineness of this material than we would be by ordinary analytical methods."

It seems therefore that ambergris is determined in a manner analogous to that of a good wine; that is, it is judged by a connoisseur, one who recognises it by general appearance, bouquet, or odour, etc., from a physical rather than from a chemical or microscopical standpoint.

Samples of the substances were sent to the leading perfumers of

*Comparison of True Ambergris, Supposed Ambergris, and Latex from Artocarpus elastica*

Substance.	Colour.	Texture.	Odour.		Melting Point.	
			Natural.	On burning.	Substance.	Ether extract.
True ambergris	Yellowish green, to brownish-black	Waxy	Earthy	Odour of burning faeces	65° C. ( $\alpha$ )	82° to 88° C. (ambrein)
"Supposed ambergris"	Mottled grey to yellow	Chewing-gum texture; yellow part is hard and brittle	Mixture of odour of brown sugar and new sawdust	Burning rubber odour	Softens at 100° C., melts at 112° C.	Softens at 100° C., melts at 120° C.
Latex from <i>Artocarpus elastica</i>	Grey	Chewing-gum texture; some parts hard and brittle	New sawdust odour	Do.	Softens at 100° C., melts at 131° C.	Softens at 100° C., melts at 118° C.

Substance.	Specific gravity.	Ether extract.		Ash.	Gutta.
		Saponification No.	Iodine No.		
True ambergris.	0.900 to 0.920	17 to 35	78	Per cent. Traces (b) 6 (c)	Per cent. —
"Supposed ambergris"	Variable; grey over 1.000; yellow less than 1.000.	109.4 to 121.4	52.9 to 78.54	3.6	21.06 (d)
Latex from <i>Artocarpus elastica</i> .	Variable, approximately 0.950.	92.50	100.17	0.54	10.00 (d)

(a) Determined in the Bureau of Science. Sixty degrees is stated by Bruff (*Chem. Abstr.*, 1916, 10, 1403) to be the melting point.

(b) Bruff, *loc. cit.*

(c) Jacob Lund, *Chem. Abstr.*, 1918, 12 773.

(d) Determined by methods given in Allen's "Commercial Organic Analysis," 4th ed., 4, 160. The sample of "supposed ambergris" was carefully selected to exclude all the brittle yellow substance. The only sample of *Artocarpus elastica* available had, however, become almost entirely crumbly (oxidised), so the gutta content is naturally low.

the United States and Europe with the request that an opinion be rendered as to whether the material was true ambergris. The replies were almost unanimous against the substance being ambergris. At this point the facts were brought to the attention of Mr. Cole. It seems that ambergris often contains "the horny gills of a cuttlefish species" (Bruff, *Chem. Abstr.*, 1916, 10, 1405) which serves as food for the whale. A careful microscopical examination proved the absence of such horny material, but led to the finding of occluded fragments of moss, leaves, and bark, so distributed as to suggest inclusion in the formation of the substance rather than foreign material gathered up after the lumps were formed. This naturally indicated a vegetable rather than an animal origin. A comparison with the samples of gums and resins at the Bureau of Forestry showed the substance to have a close physical resemblance to the latex from *Artocarpus elastica* ("Philippine Resins, Gums, and Essential Oils," *Bull. P. I. Bur. Forestry*, 1920, 20, 68. Some of the physical and chemical constants of this latex, and of the "supposed ambergris," were determined. The results are listed in the table on p. 40. The known constants of true ambergris are given for comparison.

From the data given above and the microscopical examination we are led to the conclusion that the various samples of "supposed ambergris" submitted to the Bureau of Science were neither ambergris nor of animal origin, but that they were originally derived from a tree, probably closely related to *Artocarpus elastica*.

Recently a substance which had been found in southern Palawan, near Balabac, by a Moro was submitted to the Bureau of Science for analysis. It proved to be true ambergris. (This lot of ambergris weighed 47 kg.) The material was of a waxy nature, brown, with tiny specks of white distributed through it, and there were also embedded in it many fragments of the chitinous part of the internal shell or gladius of a cuttlefish. Other chitinous fragments, in the form of a parrot's beak and the remains of the mandibles of the cuttlefish, were also found. This chitinous material is identical with the "horny gills of a cuttlefish species" referred to above. These fragments appear as thin dark brown, opaque, finely striated pieces of chitin varying in thickness from 0.04 to 0.1 mm. No moss, bark, or other vegetable material was found in the sample.

The specific gravity of the ambergris was 0.834 (? 0.934). The melting point was 65° C. The ash content was 0.21 per cent. After the ambergris was melted it remained as a brownish-black

viscous mass on cooling. Attempts to crystallise the ambrein from alcohol were unsuccessful. No crystallisable product could be obtained upon acetylation with acetic anhydride.

The above data, and especially the microscopical examination, proved that this substance was ambergris.

Mr. Cole emphasises as his conclusion that a careful microscopical examination of substances suspected of being ambergris will often prove to be of greater value in the identification of such substances than the ordinary physical or chemical methods.

**AMBRETTE, OIL OF.**—Ambrette seeds, or the seeds of *Hibiscus Abemoschus*, also known as musk seed, is a valued article in perfumery. The name *Hibiscus* is possibly derived from Ibis, the stork, a bird which is said to chew the plant. The name *Abemoschus* is derived from the Arabic *kabb-el-misk* ("grain of musk"). The plant is herbaceous, growing to about 6 to 8 feet in height, a native of the hottest parts of India. It belongs to the natural order *Malvaceæ*. Its large yellow flowers yield small grey seeds with a pronounced odour of musk, which are distilled for their essential oil. The latter is a highly aromatic liquid, of specific gravity 0.900 to 0.905, semi-solid at ordinary temperatures, the melting point varying with the quantity of free fatty acids which it contains. Samples of pure oil are sometimes quite fluid, owing to comparative freedom from palmitic acid. Farnesol has been identified as a constituent of the oil. *Schimmel & Co.* (Report, April, 1912, 23) distinguish between the normal oil and the oil deprived of its fatty acids, which is liquid at ordinary temperatures. They give the following figures for the two oils:—

	Normal oil.	Liquid oil.
Specific gravity at 15° . . . . .	—	0.9088 to 0.9123
40° . . . . .	0.891 to 0.892	—
Optical rotation . . . . .	—	+0° 14' to +1° 19'
Refractive index at 20° . . . . .	—	1.47421 to 1.47646
Acid value . . . . .	75 to 132	0 to 2.4
Ester value . . . . .	66 to 113	167.7 to 180.5
Solidifying point . . . . .	38° to 39°	—
Solubility . . . . .	Insoluble in 10 vols. of 90 per cent. alcohol.	Soluble in 3 to 6 vols. of 80 per cent. alcohol.

Laloue and Litterer (*Roure-Bertrand Fils, Bulletin*, October, 1912, 134) obtained the following figures for a normal oil :—

Specific gravity at 30°	0.8983
43°	0.8883
Optical rotation	+1° 24'
Refractive index at 30°	1.4645
Soluble in 1 volume of 90 per cent. alcohol, but a strong turbidity is produced on the subse- quent addition of the same alcohol.	
Acid value	47.0
Saponification value	195.3
"      " of the acetylated oil	213.7

**AMMONIA.**—So-called liquid ammonia, and ammonium carbonate are employed to a considerable extent in the manufacture of perfumed smelling salts. "Liquid ammonia" is a solution of gaseous ammonia,  $\text{NH}_3$ , in water, with which it forms a hydrate  $\text{NH}_4\text{OH}$ . The strongest solution of commerce has a specific gravity 0.880, and contains 35.6 per cent. of  $\text{NH}_3$  by weight. The following table gives the strength of solutions of ammonia of various specific gravities :—

Specific gravity 15° 15°	Grams $\text{NH}_3$ in		Specific gravity 15° 15°	Grams $\text{NH}_3$ in	
	100 grams	1 litre		100 grams	1 litre
	of solution.			of solution.	
0.995	1.1	11	0.935	17.1	160
0.990	2.3	23	0.930	18.6	173
0.985	3.5	35	0.925	20.2	187
0.980	4.8	47	0.920	21.7	200
0.975	6.0	59	0.915	23.3	214
0.970	7.3	71	0.910	25.0	227
0.965	8.6	83	0.905	26.6	241
0.960	9.9	95	0.900	28.3	255
0.955	11.3	108	0.895	30.0	269
0.950	12.7	121	0.890	31.7	282
0.945	14.2	134	0.885	33.7	298
0.940	15.6	147	0.880	35.6	313

Solid "ammonia" is commonly known as ammonium carbonate. It is actually a mixture of ammonium hydrogen carbonate  $\text{NH}_4\text{HCO}_3$  and ammonium carbamate  $\text{NH}_4\text{NH}_2\text{CO}_2$ . It is prepared by heating calcium carbonate with a salt of ammonia.

Commercial samples on titration should contain from 30 to 32 per cent. of  $\text{NH}_3$ .

**AMMONIACUM.**—Ammoniacum is a gum-resin obtained from the flowering stem of *Dorema ammoniacum*, a plant found in Persia and southern Siberia. The stem is pierced by beetles and the exudation induced of the milky substance contained in the ducts in the cortex. The gum-resin contains from 18 to 28 per cent. of gum, 50 to 75 per cent. of resin, and 0.5 to 2 per cent. of essential oil.

It is used to a small extent in perfumery together with opoponax. The only adulterant usually found present is the so-called African ammoniacum, the product of *Ferula tingitana*, which may be detected as follows :—

If about 60 grains are powdered and boiled for fifteen minutes with  $\frac{1}{2}$  oz. of hydrochloric acid, and the liquid cooled and filtered and then rendered alkaline with solution of ammonia, pure ammoniacum will not show any fluorescence; whilst if the African gum-resin be present, the liquid will have a blue fluorescence. Pure ammoniacum has a specific gravity 1.19 to 1.21, and the extracted resin has an acid number 69 to 80, and ester number 19 to 38.

The essential oil of ammoniacum has a specific gravity 0.885 to 0.895; optical rotation,  $+1^\circ$  to  $+4^\circ$ ; refractive index, 1.4720 to 1.4810; and ester value about 40. It contains linalyl acetate, citronellyl acetate, a dihydro-sesquiterpene termed ferulene, and a ketone termed doremone.

**AMOMIS JAMAICENSIS.**—This plant is the wild pepper of Jamaica. It yields an essential oil consisting largely of linalol. Its specific gravity is about 0.890. Attempts are being made to develop the cultivation of the plant. According to the *Bulletin of the Imperial Institute*, 1919, 3, 301, the following are the characteristics of the oil :—

Specific gravity at $15^\circ$	0.8895
Optical rotation at $22^\circ$	$-6^\circ 0'$
Acid value	2.4
Saponification value	4.2
„ „ after acetylation	129.4
Percentage of esters	1.5 per cent.
„ total alcohols $\text{C}_{10}\text{H}_{18}\text{O}$	39.4 „

It is soluble at  $15^\circ$  in 2.5 volumes of 70 per cent. alcohol; the solution becomes cloudy on the addition of 6 volumes of the same alcohol.

**AMYL ACETATE.**—This ester,  $\text{CH}_3\text{COO.C}_5\text{H}_{11}$ , is used more as a flavour than a perfume, although, judiciously used, it is very useful in the blending of fruity odours. It is the basis of artificial oil of pear, and is prepared by the esterification of amyl alcohol by acetic acid. Although usually known as amyl acetate, it is actually mainly composed of iso-amyl acetate. It has a specific gravity 0.876 and boils at  $138^\circ$  to  $140^\circ$ .

**AMYL ALCOHOL.**—The amyl alcohol found naturally in Bourbon geranium and in certain eucalyptus oils is iso-amyl alcohol, or isobutyl-carbinol  $(\text{CH}_3)_2\text{CH}(\text{CH}_2).\text{(CH}_2\text{OH)}$ . It is a liquid, boiling at  $131^\circ$ , of specific gravity 0.8135, and forms a phenyl-urethane melting at  $52^\circ$  to  $53^\circ$ . This alcohol is the principal ingredient of the amyl alcohol produced by fermentation, but this is usually a mixture with its isomers, so that the commercial esters are rarely absolutely pure chemical individuals, as they are manufactured from the fermentation product. For the characters of the esters of pure tertiary amyl alcohol  $(\text{CH}_3)_3\text{C.CH}_2\text{OH}$ , see Kondakoff (*Jour. Prakt. Chem.*, 2, 48, 467.) The commercial alcohol has a specific gravity about 0.815; refractive index, 1.4090; and boiling point,  $130^\circ$ .

**AMYL BENZOATE.**—This ester,  $\text{C}_6\text{H}_5\text{COO.C}_5\text{H}_{11}$ , is prepared by condensing amyl alcohol and benzoic acid by means of hydrochloric acid gas. It is a powerful fixative, and has a slight "amber" odour. It has a specific gravity 0.994 to 1.003; boiling point,  $261^\circ$ ; and refractive index, 1.4945.

**AMYL BUTYRATE**,  $\text{C}_5\text{H}_{11}\text{OOC}(\text{CH}_2)_2\text{CH}_3$ , is an ester of very fruity odour, used in the manufacture of fruit essences, and to a certain extent in the compounding of floral essences. The commercial article is a mixture of several isomers, of which the principal is iso-amyl butyrate. Its specific gravity is 0.866; boiling point, from  $169^\circ$  to  $180^\circ$ ; and refractive index, 1.4100.

**AMYL CAPROATE.**—This ester, also known as -amyl hexoate, is occasionally used on account of its fruity odour. It is a mixture of isomers in which iso-amyl caproate predominates. It is a liquid of specific gravity 0.864 to 0.867, and refractive index 1.4210.

**AMYL CAPYLATE.**—This ester (amyl octoate) is very similar in character to amyl caproate. It is a liquid of specific gravity 0.863, and refractive index 1.4265. It consists mainly of the iso-amyl ester.



**AMYL FORMATE.**—This ester has a sharp fruity odour. It consists mainly of the iso-amyl ester, and has a specific gravity about 0.880 and boils at 120° to 125°.

**AMYL-HEPTINE-CARBONATE.**—This body is one of a series of esters which have a peculiar, fragrant odour, and which form the basic material in the perfumes known commercially as "*vert de violette*." Their preparation is due to Moureu (French patent 306619 of 1900, American patents 749800 and 750213).

Heptene is an acetylenic hydrocarbon of the formula  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}:\text{CH}$ . It is prepared by various methods, such as from cœnanthol (heptanal), a product of the dry distillation of castor oil. This is converted into a dichloro derivative by  $\text{PCl}_5$ ; 2 molecules of  $\text{HCl}$  are withdrawn successively by aqueous and by dry caustic soda, leaving heptene. (*Vide* "Heptene Carbonate.")

Heptene is transformed into heptene-carbonic acid by treatment with magnesium ethyl bromide and passing a current of carbonic acid gas through the mixture. The heptene-carbonic acid is liberated from the magnesium salt thus formed by dilute sulphuric acid. It has the formula  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}:\text{C}.\text{COOH}$ . It is a liquid of specific gravity 0.969. It is converted into its esters by warming with the corresponding alcohol and a small quantity of strong sulphuric acid. Amyl-heptene-carbonate boils at 147° to 150° at 20 mm. pressure. The methyl ether boils at 105° to 109° at 20 mm., the ethyl ether at 114° to 117° at 18 mm., and the benzyl ether at 184° to 190° at 18 mm.

**AMYL HEPTYLATE.**—This is a fairly new and very expensive synthetic perfume. Its formula is  $\text{CH}_3(\text{CH}_2)_5\text{COOC}_5\text{H}_{11}$ . It is an oil with a very powerful fruity odour, and must be used in very small quantities, as otherwise its odour will spoil the preparation it is intended to improve. Its purity may be controlled by saponifying and examining the resulting fatty acid, which should melt at  $-10^\circ$  and boil at 223°.

**AMYL PHENYLACETATE.**—This ester has a sweet floral and fruity odour. Its specific gravity is about 0.980; refractive index, 1.4845; and boiling point about 265°. It consists mainly of the iso-amyl ester.

**AMYL PROPIONATE.**—This ester resembles the acetate in general characters. It consists mostly of the iso-amyl ester, and has a specific gravity 0.873 and boils at 150° to 163°.

**AMYL SALICYLATE.**—This is an exceedingly popular synthetic perfume. It is used to a considerable extent in the preparation of perfumes of the orchid, clover, and carnation types. It is sold under such names as “artificial orchid,” “orchidée,” or “trèfle.” The experienced perfumer will prefer to buy a pure amyl salicylate and dilute or blend it to his own taste.

It is prepared by the esterification of amyl alcohol by salicylic acid, using sulphuric acid as the condensing reagent. It is a colourless oil of delightful odour, having a specific gravity 1.055; refractive index, 1.5050; and boiling point, 278°.

**AMYL VALERIANATE.**—This ester,  $C_4H_9.COO.C_5H_{11}$ , is prepared in a similar manner to that used for the other amyl esters. It has a powerful apple odour, and is only used in small quantity in the preparation of fruity odours. It boils at 188° and is actually the iso-valerianate, or consists mainly of this variety. Its specific gravity is about 0.864, and refractive index 1.4120.

**AMYRIS BALSAMIFERA, OIL OF.**—The botanical origin of the so-called West Indian sandalwood oil was quite unknown until Holmes, Kirkby, and Petersen (*Pharm. Jour.*, 1886, iii., 16, 757, 821, 1065) decided that the plant from which it was distilled could not be considered as belonging to the natural order *Santalaceæ*. At the suggestion of E. M. Holmes, *Schimmel & Co.* obtained flowering branches of the tree from Venezuela, and an examination of these led Holmes to the conclusion that the plant belonged to the natural order *Rutaceæ*. He assumed it to be an unknown species, and named it *Schimmelia oleifera*. It is now agreed, however, that it belongs to the species *Amyris*, and the tree is now known as *Amyris balsamifera*. The wood of this tree yields from 1.5 to 3.5 of essential-oil on distillation. It is a viscid oil of heavy aromatic odour, resembling to some extent that of the true sandalwood oil. Its characters are as follows:—

Specific gravity	. . .	0.950–0.972
Optical rotation	. . .	+ 19° to + 30°
Refractive index	. . .	1.5080–1.5145
Acid value	. . .	1–3
Ester value	. . .	1–6
Ester value after acetylation	. . .	66–125

The oil contains from 27 to 55 per cent. of a mixture of alcohols of the formula  $C_{15}H_{26}O$ . This mixture was believed by Von Soden (*Pharm. Zeit.*, 1900, 45, 229) to be a single compound, and was by him named amyrol. Von Soden and Rojahn (*Pharm. Zeit.*, 1900, 45, 878), however, then found that it was a mixture

from which at least two alcohols could be isolated. These were found to have the following characters:—

Formula . . . . .	$C_{15}H_{26}O$	..	$C_{15}H_{24}O$
Specific gravity . . . . .	About 0.987	..	—
Optical rotation . . . . .	+ 36°	..	0°
Boiling point . . . . .	299°	..	Below 299°

The oil also contains a body of the formula  $C_{14}H_{12}O_3$ , melting at 117°, which has been named amyrolin; *dextro*-cadinene, and  $\beta$ -caryophyllene.

The oil is used in the cheaper types of perfumed soap, etc., where an odour resembling that of sandalwood oil is desired.

**AMYROL.**—Amyrol is probably not an individual chemical compound, but a mixture of alcohols which form the principal odour bearer of the so-called West Indian sandalwood oil. This oil is distilled from the wood of *Amyris balsamifera* (*vide* "Sandalwood Oil."). The mixture of alcohols has the following characters: specific gravity, 0.980 to 0.982; optical rotation, + 27°; and boiling point, 299° to 301° at 748 mm. Van Sodan and Rojahn (*Pharm. Zeit.*, 1900, 45, 229) claim to have separated this mixture into two isomeric alcohols, having either the formula  $C_{15}H_{24}O$  or  $C_{15}H_{26}O$  and the following characters:—

Formula . . . . .	$C_{15}H_{26}O$	..	$C_{15}H_{24}O$
Specific gravity . . . . .	0.987	..	—
Optical rotation . . . . .	+ 36°	..	0°
Boiling point . . . . .	299°	..	Below 299°.

**ANDROL.**—This body is an alcohol, isomeric with citronellol, found in oil of water fennel.

**ANDROPOGON IWARANCUSA.**—This essential oil has been investigated by J. L. Simonsen (*Jour. Chem. Soc.*, 1921, 1644). It is of interest in that it was found to contain about 80 per cent. of piperitone, the ketone discovered by Smith in certain eucalyptus oils (see "Piperitone"). The grass occurs in the Himalayas and outer hill zone from Kashmir to Assam, ascending to 8,000 feet and above, and in the plains from north-west Himalaya to Bombay Presidency. The piperitone present is dextrorotatory.

**ANDROPOGON OILS.**—The principal oils distilled from plants of the natural order *Gramineæ* belong to the family formerly known as *Andropogon*. Much confusion had crept into the nomenclature of these plants, but it has been dissipated by Dr. Otto

Stapf (*Kew Bulletin*, 1908, 8, 297), who has rearranged the classification, with general approval and acceptance. (See under "Grass Oils (Perfumed) of India and Ceylon," "Cymbogon," "Lemongrass," "Citronella," "Vetivert," "Palmarosa," etc.)

**ANETHOL.**—Anethol  $C_{10}H_{12}O$  (iso-estragol, Methyl-*para*-oxypropenyl-benzene) is the principal constituent of aniseed and star aniseed oil, and is also present to a large extent in oil of fennel. It is a crystalline body, melting at  $22^{\circ}$  to  $23^{\circ}$ , of specific gravity 0.985 at  $25^{\circ}$ ; refractive index, 1.5600 at  $25^{\circ}$ ; and boiling point,  $234^{\circ}$ . It is used to a limited extent in perfumery, but is of most importance in the preparation of anisic aldehyde, a body generally known as aubepine (*q.v.*), the basic material for the preparation of the hawthorn type of perfume.

**ANGELICA OIL.**—All parts of the Umbelliferous plant *Angelica officinalis* (*Angelica Archangelica*) yield essential oils. The principal of these is that obtained from the fresh root. The plant is found in Lapland, Sweden, Norway, Germany, etc., and is cultivated to a considerable extent in Saxony. The oil is used in the flavouring of liqueurs, etc., and to a small extent in perfumery. It usually has a specific gravity 0.855 to 0.920; optical rotation,  $+16^{\circ}$  to  $+40^{\circ}$ ; refractive index, 1.4770 to 1.4880; and ester value, 12 to 40. *Roure-Bertrand Fils* (*Bulletin*, October, 1921, 34) have distilled an oil from the fresh roots which had a specific gravity 0.8907; optical rotation  $+6^{\circ} 42'$ ; and ester number, 45. The flavouring constituents are not well understood. Japanese angelica oil is obtained from *Angelica anomala*, and has a slight odour of musk.

**ANISEED.**—Two entirely different plants, belonging to different natural orders, yield aniseed oils which are practically identical. The true aniseed oil is obtained from the fruits of *Pimpinella Anisum* (N.O. *Umbelliferae*). The so-called star aniseed oil, which forms the bulk of the world's supply, is the product of the fruit of *Illicium verum* (N.O. *Magnoliaceae*). Except for the fact that the oil from the true aniseed is rather more delicate in odour, the two oils may be regarded as identical. They are used for flavouring to a considerable extent, and to a small extent in perfumery. The chief value, however, of aniseed oil to the perfumery industry lies in the fact that it provides the raw material for the manufacture of aubepine.

The star anise (*Badiane*) is chiefly found in southern China and Tonkin. The oil is distilled, principally by natives, and sold to

merchants, who transfer it to Hong Kong, where it is bought by exporters and sent thence to Europe and America. Adulteration was at one time very extensively practised, chiefly by a group of Chinese merchants who were known as the *Bande Noir*, but to-day the oil reaches Europe in a state of purity, and is seldom adulterated. The process of distillation is as follows. About 20 lb. of the fruit are placed in an iron pan and covered with water. A second iron pan is placed upon this, upside down, so as to form a cover. The latter vessel is pierced with a circular opening, over which is placed an earthen vessel with three small orifices in the lower part, which allow the access of vapour. These orifices are covered on the inside by small ear-shaped hoods, which cause the vapour to be spread over the sides of the vessel. This earthen vessel is covered with an iron pan, which acts as a refrigerator and into which a continuous current of cold water is admitted. The joints of the first two iron pans are luted, and the earthen vessel and refrigerator are jointed with cloth bandages. The vapour reaches the earthen vessel and is condensed when it impinges against the refrigerator, and falls into a circular trough at the bottom of the vessel, whence it escapes through a small pipe. The annual exportation of star aniseed oil varies from 60,000 to 200,000 kg. per annum.

*Illicium verum* is a small tree, growing to the height of from 8 to 15 metres. The trunk, which is frequently bifurcated at the base, is from 25 to 30 cm. thick, and rises to a height of 1.5 to 2 metres without branching. The leaves are evergreen, the flowers appear twice a year, and the young fruits are star shaped, which gives the name to the tree. The yield of oil varies from 2.5 to 5 per cent. The essential oil is, at ordinary temperatures, a solid crystalline mass having the following characters: specific gravity at 20°, 0.980 to 0.990; optical rotation, + 1° to - 2°; refractive index, 1.5530 to 1.5565; melting point, 16° to 19°; congealing point, 15° to 17.5°.

The true aniseed, *Pimpinella Anisum*, is found in many parts of Europe, principally, however, in Russia. According to *Schimmel & Co.*, the following yields are obtained from the fruit as grown in various countries:—

			Per cent.
<i>Chili</i>	1.9 to 2.6	<i>Italy</i>	2.7 to 3.5
<i>Macedonia</i>	2.2	<i>Moravia</i>	2.4 to 3.2
<i>Mexico</i>	1.9 to 2.1	<i>East Prussia</i>	2.4
<i>Russia</i>	2.4 to 3.2	<i>Spain</i>	3.0
<i>Syria</i>	1.5 to 6.0	<i>Thuringia</i>	2.4

## P E R F U M E R Y

In Russia anise is grown in the county of Voronetz in the districts of Biriutch, Ostrogojsk, and Valuiki, and the oil is, as mentioned above, practically identical with star anise oil.

The following bodies have been identified in star aniseed oil: *dextro*-pinene, phellandrene, cymene, cineol, dipentene, limonene, terpineol, methyl-chavicol, hydrokinone-ethyl-ether, safrol, a sesquiterpene, anise ketone, and anethol. True aniseed oil has not been so exhaustively investigated, and the only bodies so far detected are anethol, methyl-chavicol, anise-ketone, and aldehyde.

The fruit of a plant *Seseli Harveyanum*, known in Victoria (Australia) as aniseed (but which more closely resembles fennel), has been examined by Umney and found to contain anethol, but in considerably less quantity than ordinary aniseed oil. There is also a false aniseed, *Illicium religiosum*, known in Japan as *Shikimi-no-ki*. It contains eugenol, cineol, safrol, and a mixture of terpenes. The principal adulterant of aniseed oil is petroleum oil. The pure oil is soluble in 3 volumes of 90 per cent. alcohol, a feature which is interfered with by the presence of petroleum. So long as the congealing and melting points of the oil fall within the limits given above, it is most unlikely that the oil is adulterated. It must be remembered, however, that aniseed oil is one of those oils with a considerable tendency to remain in a state of superfusion, so that it may be cooled down to well below its congealing point without becoming solid. To determine these temperatures, a small quantity of the oil should be placed in a narrow test-tube and cooled down to about 10°. If it does not congeal on stirring with a small-bulbed thermometer, a crystal of anethol should be added, when the mass will rapidly crystallise. It should be gently stirred, and the temperature rises as crystallisation takes place. The maximum temperature is noted, and is taken as the congealing point. The tube is then gently warmed by holding in the hand, and the contents kept stirred all the while by the thermometer. The temperature at which the crystals completely disappear is taken as the melting point. Oils with congealing points of 12° to 13°, but which are soluble in 90 per cent. alcohol, are not likely to be adulterated with petroleum, but may be adulterated with a fraction of camphor oil, or by the abstraction of anethol. An oil adulterated in this manner has been examined by E. J. Parry (*Chemist and Druggist*, 1910, 687). Its characters, compared with those of a pure oil, were as follows:—

	Adulterated.	Pure.
Specific gravity at 20°	0.972	0.982
Optical rotation	0°	—1° 10'

## P E R F U M E R Y

	Adulterated.		Pure.
Refractive index at 20° . . . . .	1.5469	..	1.5547
Melting point . . . . .	13°	..	18°
Congeaing point . . . . .	11°	..	15°
Refractive index of first 10 per cent. distilled . . . . .	1.516	..	1.5346
Refractive index of last 20 per cent. . . . .	1.540	..	1.556

**ANISIC ALCOHOL.**—This alcohol  $C_6H_4(CH_2OH)(OCH_3)$  has been found as a constituent of Tahiti vanilla beans. It is produced artificially by the action of caustic potash on anisic aldehyde. It forms colourless crystals melting at 45°, and boiling at 259°. It forms a phenyl-urethane melting at 93°.

**ANISIC ALDEHYDE.**—This artificial perfume is known commercially as aubepine, or artificial hawthorn. It is a methyl ether of *para*-oxy-benzaldehyde, of the formula  $C_8H_8O_2$ . It is an oil having the following characters: specific gravity, 1.1275; optical rotation, 0°; refractive index, 1.5730; and boiling point 246°.

Anisic aldehyde is the basic material for all perfumes of the "may blossom" type.

A small amount is obtained as a by-product in the manufacture of coumarin, but it is usually manufactured on a commercial scale by the following process. Star aniseed oil is warmed for an hour or two with three times its volume of nitric acid (specific gravity, 1.1), and the heavy oil separating is washed with potash solution. This oil is crude anisic aldehyde. It is combined with sodium bisulphite by shaking it with a hot solution of that salt, and the resulting crystals are washed with alcohol, dried on porous paper, and dissolved in water. It is then warmed with solution of sodium carbonate, and the resulting anisic aldehyde is separated and rectified.

Aubepine is also manufactured commercially by treating toluene sulphonic chloride, a by-product in saccharine manufacture, with a solution of soda ash at 100°. The *p*-toluene sulphonate of sodium resulting is melted with caustic potash, and the resulting *para*-cresol liberated by hydrochloric acid; this is then esterified with dimethyl sulphate, and the resulting *para*-cresol methyl ether is directly oxidised to anisic aldehyde.

The solid aubepine of commerce is the combination of the aldehyde with sodium bisulphite, but is now seldom employed.

**ANISYL METHYL KETONE.**—See "Methoxy-acetophenone."

**ANTHRANILIC ACID ESTERS.**—Anthranilic acid, or ortho-amido-benzoic acid  $C_6H_4 \cdot NH_2 \cdot COOH$  is one which forms several highly odorous esters, of which the most important naturally occurring compound is methyl anthranilate  $C_6H_4 \cdot NH_2 \cdot COOCH_3$ . The only other ester of any particular importance is ethyl anthranilate. Methyl-anthranilic acid also yields similar esters, of which the methyl ester occurs naturally.

Methyl anthranilate is found in the essential oils of neroli petitgrain, jasmin, gardenia, and tuberose, frequently associated with methyl methyl-anthranilate.

Anthranilic acid is manufactured on a commercial scale by first oxidising naphthalene by means of fuming sulphuric acid in the presence of salts of mercury. Forty grams of mercury are dissolved in 1 kg. of sulphuric acid, and the mixture is heated until the sulphuric acid distils. To this is gradually added a mixture, prepared three hours previously, of naphthalene 3.5 kg., sulphuric acid (66° B.) 37 kg., and fuming sulphuric acid 10.5 kg. The phthalic anhydride formed distils over with some sulphuric acid, from which it is freed by washing. It is finally sublimed, when it should melt at 128°.

Phthalic acid is melted and brought to a temperature of 140°. A current of dry ammonia gas is then passed through it, the reaction temperature being gradually increased to 240°. This results in the formation of phthalimide  $C_6H_4(CO)_2NH$ . Phthalimide is treated with potassium hypobromite or hypochlorite in the presence of excess of alkali, and anthranilic acid results. On recrystallisation the pure acid melts at 144° to 145°. There are several other methods by which this acid can be obtained, but the above is the most practical. The acid is esterified with methyl or ethyl alcohol, as the case may be, using hydrochloric acid as the condensing agent.

Methyl anthranilate  $C_6H_4(NH_2)COO \cdot CH_3$  is a crystalline body melting at 24°, and boiling at 135° at 15 mm. Its specific gravity is 1.168. Ethyl anthranilate is a liquid boiling at 145° at 20 mm. Both esters have a characteristic neroli odour, that of the ethyl ester being sweeter and softer.

If methyl anthranilate be heated with methyl iodide and water for several hours under a reflux condenser, methyl methyl-anthranilate, melting at 18°, results.

F. B. Power (*Jour. Amer. Chem. Soc.*, 1921, 43, 377) has published a method for the detection of methyl anthranilate in fruit juice, in which 500 c.c. of the juice are steam distilled



until 200 c.c. have come over, when, if appreciable quantities of methyl anthranilate are present, the solution will show a bluish fluorescence. At this stage the ester is extracted from the distillate by three successive quantities of chloroform of 10 c.c. each. The chloroform extracts are filtered, and the solutions evaporated on the water bath. Two cubic centimetres of 10 per cent. sulphuric acid solution are added to the residue, and the mixture is transferred to a test-tube. During the evaporation of the chloroform extracts, etc., there is prepared a mixture of 1 c.c. of 0.5 per cent. pure beta-naphthol solution, 1 c.c. of 10 per cent. solution of sodium carbonate monohydrate  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , and 1 c.c. of a 10 per cent. solution of caustic soda. On adding the ester solution in the test-tube to this mixture, the presence of 0.1 mg. or more of the methyl anthranilate will be shown by the formation of yellowish-red coloration.

Another method is to add a drop of dimethylaniline to the ester solution, and, when solution results, the addition of a slight excess of caustic soda will give a yellow coloration, which is changed to red by the addition of a little dilute acid.

The quantitative determination of methyl anthranilate is best carried out by the method suggested by Hesse and Zeitschel. From 25 to 30 grams of the sample are dissolved in two to three times its volume of perfectly dry ether. The mixture is then cooled in a freezing mixture, and then a mixture of 1 volume of sulphuric acid and 5 volumes of ether is added slowly until no further precipitation takes place. The whole of the methyl anthranilate is thus precipitated as sulphate. The precipitate is collected, washed with ether and weighed. This gives the approximate amount of the ester present. For a more exact result, the precipitate may be titrated with semi-normal potash solution. If P be the weight of oil employed and N be the number of cubic centimetres of semi-normal alkali used, then the percentage of methyl anthranilate is given by the formula

$$\frac{3.775 \times N}{P}$$

A. G.

**AQUILARIA CRASSNA.**—This plant, growing principally in Cambodia, is liable to be infected with a disease, the nature of which is not yet understood, which causes the wood to become resinous and highly odorous, especially when burned. The wood is used in the preparation of Chinese joss sticks, and for incense purposes generally. (*Vide La Parfumerie Moderne*, 1923, 124.)

**ARMENIAN PAPER.**—The so-called Armenian paper is an absorbent paper saturated with an aromatic solution and dried so that, when burned, it evolves an odour of the type of incense. The paper is made by making an alcoholic solution of the following type :—

Frankincense	. . . . .	2 parts.
Storax	. . . . .	2 „
Gum benzoin	. . . . .	2 „
Balsam of Peru	. . . . .	0.5 part.
Balsam of tolu	. . . . .	0.5 „
90 per cent. alcohol	. . . . .	5 parts.

To this is added sufficient of a saturated solution of potassium nitrate in water to enable the paper to burn freely, and the absorbent paper is then soaked in the mixture, drained, allowed to dry in the air, and cut into convenient strips.

**AROMADENDRAL.**—This body is an aldehyde of the formula  $C_9H_{12}O$ , isolated by Baker and Smith from various oils of eucalyptus. It has a pleasant odour, resembling that of cumic aldehyde, with which *Schimmel & Co.* consider it to be identical. It has a specific gravity about 0.950 and boils at about  $218^\circ$ .

**ARTEMISIA OILS.**—Certain of the oils distilled from species of *Artemisia* (N.O. *Compositæ*) are used to a considerable extent in flavouring, and to a small extent in perfumery. The principal of these is the oil of *Artemisia Absinthium*, oil of wormwood or oil of absinthe. The plant is indigenous in the Old World as far north as Scandinavia, Finland, and Siberia, and appears to have migrated to North America. It is found wild in some parts of Great Britain, and is cultivated in the United States, Russia, Algeria, Corsica, Spain, and Italy. The principal areas under cultivation in the United States are situated in Wayne County and in Sauk County.

The characters of the oil vary considerably, according to whether the herb is fresh or dry or in an intermediate condition.

It is a somewhat viscid liquid, usually of a dark green or blue colour, but sometimes dark brown. The colour appears to be dependent on the length of time taken by the distillation.

Gildemeister and Hoffmann (2nd English ed., vol. 3, p. 640) give the following figures for genuine samples of the oil as found in commerce :—

# P E R F U M E R Y

	French.	Algerian.	Italian.	American.
Specific gravity.	0.901—0.954	0.905—0.939	0.918—0.943	0.916—0.938
Refractive index	1.46684	—	—	—
Acid value	Up to 6.7	Up to 6.1	Up to 5.6	Up to 2.2
Ester value	11 to 108	14 to 93	15 to 37	46 to 89
Ester value after acetylation	—	—	123.2	113.9

*Schimmel & Co.* distilled a number of specimens of the herb grown at Miltitz and at Barrême, and give the following results for the oils obtained :—

## *Miltitz*

Variety of Herb.	Hungarian.	Miltitz.	French grown in Miltitz.
Specific gravity	0.8845—0.9125	0.932—0.954	0.927—0.933
Acid value	16.8	0.2—8.6	Up to 1.5
Ester value	35—75.4	76—85	38.8—65.3
Ester value after acetylation	—	153—222	93.3—170.3

## *Barrême*

Variety of Herb.	Wild.	Cultivated.
Specific gravity	0.901—0.908	0.936—0.939
Acid value	Up to 3.2	Up to 2.8
Ester value	34.3—57.4	96.4—114
Ester value after acetylation	—	164.5

An oil distilled from wild Dalmatian herb had a specific gravity 0.9188 ; acid value, 1.3 ; and ester value, 64.6 (*Schimmel & Co.*, Report, October, 1911, 101).

E. R. Miller (*Bulletin Univ. Wisconsin*, 693) has examined six samples of Wisconsin oils, and found them to contain from 25.8 to 35.1 per cent. of esters calculated as thujyl acetate, and from 8.9 to 21.6 per cent. of free alcohols as thujyl alcohol.

Charabot (*Comptes Rendus*, 1900, 130, 923) has shown that the proportion of thujone to thujyl alcohol in the oil changes as the plant develops, the thujone being gradually converted into thujyl alcohol.

# P E R F U M E R Y

*Roure-Bertrand Fils (Bulletin, April, 1906, 36)* give the following results from two oils distilled from wild plants grown in the hills round about Caussols (Alpes Maritimes):—

	1. Per cent.	2. Per cent.
Esters . . . . .	9.0 ..	5.5
Combined alcohols . . . . .	7.0 ..	4.3
Free alcohols . . . . .	71.9 ..	76.3
Thujone . . . . .	8.4 ..	3.0

The oil contains, in addition to thujyl alcohol and its esters, thujone, phellandrene, cadinene, traces of pinene, and a blue compound known as azulene. The thujone present exists in two isomeric modifications.

*Artemisia arborescens* is a shrub-like plant common to the Mediterranean countries. *Schimmel & Co. (Report, November, 1908, 136)* have examined a sample of the oil which had a deep blue colour. Its specific gravity was 0.9458; acid value, 9.8; and ester value, 19.5. *Jona (Ann. Chim. Applic., 1914, 1, ii, 63)* found 14 per cent. of alcohols present, including thujyl alcohol and borneol, and 13 per cent. of thujone.

*Pellini and Morini (Riv. Ital. del Essences et del Prof., December, 1923)* give the following characters for this oil:—

	Sicilian.	Sardinian.	Calabrian.
Specific gravity . . . . .	0.9578	0.9458	0.943
Acid number . . . . .	15	9.8	10.5
Ester number . . . . .	11.9	19.5	14.33
Ester number after acetylation . . . . .	28.6	50	47.6
Ester per cent. . . . .	4.17	6.82	—
Free alcohols per cent. . . . .	4.65	8.58	—
Total alcohols per cent. . . . .	7.92	13.94	13.08
Yield per cent. . . . .	0.482	0.570	0.200

*Artemisia vulgaris* is a common weed, which grows along hedges and road sides, and which yields about 0.1 per cent. of essential oil of specific gravity 0.907. It contains cineol. It appears, however, that this oil differs greatly in character, according to its place of origin. Two samples, known as yomugi oil in Japan, which were probably derived from *A. vulgaris*, were examined by *Schimmel & Co. (Report, October, 1903, 78; April, 1904, 78)*, and found to have the following characters:—

Specific gravity . . . . .	0.910	0.9126
Optical rotation . . . . .	— 13° 16'	— 18° 50'

## P E R F U M E R Y

Refractive index	1.4776	..	1.4857
Acid value	1.56	..	1.32
Ester value	29.8	..	16.2

An oil examined at the Imperial Institute under the name Ngai Yau, received from Hong Kong, was also probably derived from the same plant. It had a specific gravity 0.939; saponification value, 103.3; and saponification value after acetylation, 205.9.

Indian wormwood oil, also probably derived from *A. vulgaris* (*A. Indica*, Willd.), has been examined, and found to have the following characters:—

	1.	2.
Specific gravity	0.922	0.949 (at 26°)
Optical rotation	— 8° 52'	+ 57° 2'
Refractive index	1.4620	—
Acid value	1.2	—
Ester value	22.1	99
Ester value after acetylation	55.5	228

(See also *Schimmel's Report*, November, 1908, 140.)

*Artemisia Barrelieri*.—The essential oil from this plant is used in the manufacture of Algerian absinthe. It has a powerful aromatic odour. It has a specific gravity 0.923, and consists mainly of thujone.

*Artemisia Glutinosa*.—Bennett (*P. & E. O. R.*, 1920, ii., 286) has examined the essential oil distilled from this plant, which grows freely in Spain. It has a strong aromatic odour recalling that of a mixture of sage, rosemary, and spike lavender. The oil contains terpenes, methyl-chavicol, cineol, and borneol. It has the following characters:—

Specific gravity	0.937
Optical rotation	+ 24°
Refractive index	1.4780
Total alcohols as borneol	17.5 per cent.
Esters as bornyl acetate	6.3 „
Phenols	8 „
Aldehydes and ketones	18 „

For other artemisia oils, see E. J. Parry, "The Chemistry of Essential Oils, etc." (4th ed., vol. 2, p. 291). See also "Tarragon Oil," "Gougat, Oil of," and "Schich, Oil of."

**ARTIFICIAL ESTERS IN ESSENTIAL OILS.**—The term "artificial esters" is usually applied to esters that are artificially prepared, and are often added to essential oils in order to raise the ester value of the oil.

acetate in essential oils by a method in which the glycerol is separated and weighed.

*Terpinyl Acetate*.—This ester is hydrolysed with greater difficulty than the usual natural esters present in essential oils, and *Messrs. Schimmel* (*Schimmel's Report*, October, 1910, p. 60) have devised a method for its detection, based on this fact.

This method is to saponify for one hour and two hours, using only half the amount of semi-normal alkali for the one-hour saponification that is used for the two hours' saponification. In the case of pure oils, the difference between one hour and the two hours' saponification values should not amount to more than 3; if 5 per cent. of terpinyl acetate is present, a difference of as much as 14 is sometimes found.

*Lauric and other Fatty Esters*.—These esters give no precipitate in Bennett's test, and as some of them are somewhat volatile in steam, they are not easily detected by *Schimmel's* method for detecting non-volatile fatty acids (*Schimmel's Bericht*, October, 1910, p. 43; April, 1911, p. 151, 1914, p. 125; *P. & E. O. R.*, 1919, p. 175).

In order to detect these esters, it is best to separate out the fatty acids, and this is carried out as follows :—

Ten cubic centimetres of the oil are saponified for one hour with 20 c.c. of 2/N alcoholic potash. Twenty-five cubic centimetres of water are then added, and the bulk of the alcohol is evaporated off. The solution is then almost neutralised to phenolphthalein, and the unsaponified oil removed by shaking out three times with ether.

The aqueous solution is then made acid to methyl orange, and shaken out with ether.

The ethereal solution will now contain acids, such as benzoic, cinnamic, oleic, phthalic, and lauric, and these will be obtained in a moderately pure condition by evaporating off the ether.

M. S.

**ASAFÆTIDA**.—This substance is a foul-smelling gum-resin which, in an extremely diluted condition, is of value both as a flavour and as a perfume. It is obtained as an exudation from the cortex of the stem and root of various species of *Ferula*, principally *F. foetida*, *F. scorodosma*, and *F. narthex*. Its popular name is "Devil's dung." It is used in the form of a tincture in 70 per cent. alcohol. Its principal constituent is the ferulic ester of asaresinotannol. A good sample should not contain more than 10 per cent. of ash (earthy matter), the best samples containing from 3 to 5 per cent. It yields an essential oil consisting principally

of allyl sulphides, and having a specific gravity 0.915 to 0.993; optical rotation,  $+10^{\circ}$  to  $-36^{\circ}$ ; and refractive index, 1.4940 to 1.5260. (Refer Umney and Bunker, *P. & E. O. R.*, 1910, 165.)

**ASARUM CANADENSE, OIL OF.**—The rhizomes of the Canadian snakewood plant (*Asarum canadense*) yield 3 to 5 per cent. of essential oil having a specific gravity 0.950 to 0.952; optical rotation,  $-2^{\circ} 50'$  to  $-10^{\circ} 40'$ ; and refractive index, 1.4850 to 1.4890. It contains pinene, linalol, borneol, terpineol, geraniol, methyl-eugenol, fatty acids, and a lactone of unknown constitution. Its odour is pungent and aromatic, recalling patchouli and ginger. It is used in the United States for giving a spécial "note" to eau de Cologne.

**ATTAR OF ROSE.**—See "Rose."

**AURANTIENE.**—This name is given to the terpenes of orange oil, produced in the manufacture of terpeneless orange oil. It consists of limonene, principally in the dextrorotatory form.

**BACKHOUSIA OILS.**—*Backhousia citriodora*, a small tree growing in Queensland, yields about 1 per cent. of an essential oil of pleasant verbena odour, which is used in perfumery to some extent, but which is now only produced on a small scale, owing to the fact that lemongrass oil, which it closely resembles, is sold at a cheaper rate. The oil contains from 90 to 95 per cent. of citral (*vide* "Ionone"). It has a specific gravity 0.895 to 0.900, refractive index 1.4860 to 1.4889, and is optically inactive.

*Backhousia myrtifolia* also yields a pleasant-smelling essential oil, of which the principal constituent is the phenol ether elemicin. It has a specific gravity 1.026 to 1.057.

*Backhousia angustifolia* yields an essential oil of pleasant odour, which contains about 60 per cent. of a body which is probably a phenol allied to tasmanol and leptospermol. It has been investigated by A. R. Penfold, of the Technological Museum, Sydney (*Jour. Roy. Soc. N.S.W.*, 57, 300). A yield of 1.05 per cent. on the dried leaves and terminal branchlets was obtained. The oil is of particular interest, since it differs materially from any *Backhousia* oil hitherto described, and contains about 75 per cent. of a hitherto undescribed body, which appears to be a phenol. Dextro- $\alpha$ -pinene,  $\beta$ -pinene, cineol,  $\alpha$ -terpineol, sesquiterpenes, and a solid body—probably a lactone—melting at  $118^{\circ}$  to  $119^{\circ}$  were also identified in the oil. The principal constituent is a somewhat remarkable compound, and appears to belong to

# P E R F U M E R Y

the group of bodies of which tasmanol and leptospermol are recognised constituents. Penfold classes it tentatively as a phenol. Four oils also examined had the following characters :—

	1	2	3	4
Specific gravity .	1.0414	1.0272	1.0042	0.9599
Optical rotation .	+ 1.55°	0°	— 1.2°	+ 0.6°
Refractive index .	1.5086	1.4973	1.4886	1.4790
Acid number . . .	203	198.3	—	—
Ether number . . .	216.6	207.1	181.1	—
Ester number after acetylation . . .	225.7	257.1	213.1	—
Phenols . . . . .	75 per cent.	75 per cent.	60 per cent.	26 per cent.

After extracting the phenols with a caustic soda solution, the non-phenolic residues resembled eucalyptus oil in odour, and had the following characters : specific gravity, 0.903 to 0.908 ; optical rotation, + 6.1° to + 8.25° ; refractive index, 1.4655 to 1.4668 ; cineol, 30 to 50 per cent. This portion of the oil was used for the determination of the various constituents mentioned above. The stearoptene was crystallised from alcohol, and melted at 118° to 119°. The formula appears to be  $C_{15}H_{16}O_5$ , which was confirmed by cryoscopic determination of the molecular weight. The phenolic constituent is a viscous liquid, giving a brilliant orange colour with ferric chloride, and is slightly lævorotatory. Its formula is probably  $C_{10}H_{14}O_3$ , and its characters are given in the following table. Four different specimens are included from different sources, and obviously traces of impurities are present in some of them, especially No. 1.

	1	2	3	4
Boiling point, 10 mm. . . .	122°–124°	123°–125°	123°–124°	122°–124°
Specific gravity . .	1.1054	1.0900	1.0848	1.0885
Optical rotation . .	— 0.55°	— 4.65°	— 4.65°	— 4.45°
Refractive index . .	1.5288	1.5130	1.5084	1.5113

*Backhousia sciadophora* yields an oil of specific gravity about 0.880, and optical rotation + 34°. It consists in the main of pinene (80 to 85 per cent.), a sesquiterpene, a sesquiterpene alcohol, a phenol, and caprylic acid in the form of esters.

**BALM OF GILEAD.**—This balsam, also known as Mecca balsam, is the product of *Balsamodendron Gileadense* or *B. Opo-*



*balsamum*; the former plant probably being a variety of the latter. The tree is found principally in Arabia. An interesting historical account of it is given by de Sacy ("Relation de l'Egypte," Paris, 1810). It was cultivated—and it is very difficult to cultivate—in a garden at Matriya, near Cairo, from the eleventh up to the seventeenth century, where it was so valued that the garden was completely walled in and was guarded by janisaries. Abd-ul-Latif (*obit.* 1231) gives an account of the preparation of the balm. Incisions were made in the bark down to the wood (apparently to injure the cambium cells and induce a pathological secretion), and the juice exuding was scraped from the tree and preserved in bottles, which were buried in the earth for a time, and afterwards exposed to the sun until the balsam had separated from the impurities. It was then subjected to some secret process, and finally stored in the royal treasury. In 1550 only nine or ten trees remained alive in this garden, and no balsam was yielded by them. The last tree perished in 1615 through an inundation of the Nile. It now grows in Arabia, in the neighbourhoods of Medina and Mecca. About the beginning of April the trees drop their juice from cuts made in the smaller branches. An inferior balsam results from boiling the twigs and skimming off the floating material from the water.

The genuine balsam, which is very rarely found in commerce, is at first turbid and white, but thickens with age and becomes of a honey colour. It is adulterated with turpentine, Chian turpentine, Canada balsam, and common rosin. Having a low acid value, it does not solidify when triturated with an eighth part of its weight of magnesia, as do most of the pine resins. A reasonably fresh, pure Mecca balsam should have an acid number of about 40, and an ester number about 100. It is used in the manufacture of some Oriental perfumes.

**BALM, OIL OF.**—Oil of balm, or melissa oil, is distilled from the herb *Melissa officinalis*, a plant belonging to the natural order *Labiatae*. It is a native of western Asia, and is fairly widely distributed. The name is derived from the Greek *melissa*, a bee, and is indicative of the attraction the flowers have for bees on account of the saccharine matter they produce on a considerable scale, and which suits the bees for the secretion of honey. The leaves have a pleasant odour recalling lemongrass and citronella. The essential oil is scarcely a commercial article in the pure state, as the yield obtained will not allow the oil to be sold remuneratively. It is a liquid of specific gravity about 0.895 to

0-925, and contains citral, citronellal, geraniol, linalol, and citronellol. The oil of balm of commerce is either lemon oil distilled over melissa leaves, with a little citronella oil added, or the melissa leaves are omitted and the oil is entirely factitious.

**BALSAMS.**—The term “balsam” is an inexact and elastic one, and is incapable of scientific definition. From the point of view of the perfumer, the aromatic balsams may be taken to be oleoresinous exudations of plants, sometimes normal, sometimes pathological, often containing only very little essential oil, but always containing odoriferous constituents, most frequently benzoic or cinnamic acids or their esters. Commercially the term is usually restricted to *exudations* from the plant, but scientifically there is no reason to distinguish between these exudations and aromatic oleoresins extracted from the plant by solvents. Such bodies are benzoin, storax, balsam of Peru, balsam of Tolu, labdanum, etc., all natural exudations; and such bodies as oak moss or orris resin, oleoresins obtained by extraction with solvents. Most of this group of bodies—indeed, practically all of them—are of the greatest value as fixatives, subject to this qualification. If an oleoresinous material has a strong and pronounced odour, it can only be used as a fixative where its odour will blend with the other perfumes used, unless it be so powerful a fixative that very small quantities can be employed. Apart, however, from this characteristic of these substances, most of them are highly odorous, usually having a heavy odour of the so-called Oriental type, for which class of perfumes they are invaluable as actual odour bearers, apart from their fixative value. (See also “Fixatives.”)

**BALSAMO BLANCO.**—This substance, known also as White balsam of Peru, is said to be obtained from the fruit pods of *Myroxylon Pereiræ*. Germann, however, states that this product differs from the white balsam of Peru which he has examined, and considers it may be identical with American storax from *Liquidambar styraciflua*. It rarely finds its way into commerce to-day.

**BALSAM OF PERU.**—This substance is of the greatest value in the preparation of heavy odours of the Oriental type. It is also much valued as a fixative. It is an oleoresinous liquid, of the consistency of a thick syrup, obtained from the trunk of *Myroxylon Pereiræ*, a leguminous tree growing in the forests of San Salvador, in South America. The secretion is not a natural one, but is pathological, being induced by the gentle heating, and

then scorching, of the bark. As the liquid exudes it is soaked up by cloth, with which the wounded places are covered. The cloths are pressed and boiled with water, and the balsamic liquid is separated, and is then ready for export.

Balsam of Peru is a dark, reddish-brown liquid of great viscosity and of a penetrating and very sweet odour. It contains from 55 to 65 per cent. of a substance known as cinnamein, which, however, is not a definite chemical individual, but is a mixture of esters of both cinnamic and benzoic acids. It also contains a small amount of free aromatic acids and alcohols, and a trace of vanillin. The alcohols combined with the aromatic acids are principally benzyl alcohol and peruvial.

When pure the balsam has a specific gravity 1.1400 to 1.612, refractive index 1.5800 to 1.5855, and contains from 50 to 65 per cent. of cinnamein, which can be estimated in the following manner. One gram is dissolved in 30 c.c. of ether and extracted twice with seminormal alkali, the alkaline solution being washed with ether and the ethereal liquids combined. The ethereal residue is dried and weighed. This residue, cinnamein, should have a saponification value of 235 or over.

There is on the market a certain amount of artificial balsam of Peru, which is of far less odour value than the natural balsam. It is stated (British Pharmaceutical *Codex*, 1923, p. 173) that this can be detected by the following reaction. Two grams of the sample are shaken with 10 c.c. of petroleum spirit, and the petroleum solution is evaporated in a porcelain dish. The residue is dried on a water bath, cooled, and mixed with 2.5 c.c. of nitric acid of specific gravity 1.38. The pure balsam gives only a golden yellow colour. Dieterich ("Analysis of Resins," Scott, Greenwood & Co., London) gives the following values for three samples of authentic origin :—

	1	2	3
Acid value . . . . .	77.46	76.92	72.34
Ester value . . . . .	165.61	137.42	137.67
Saponification value . . . . .	243.07	214.34	215.01
Cinnamein . . . . .	71.4 per cent.	77.6 per cent.	73.6 per cent.
Resin esters . . . . .	15.7 "	13.2 "	17.3 "
Insoluble in ether . . . . .	4.38 "	4.31 "	3.57 "

**BALSAM OF TOLU.**—Balsam of tolu is an aromatic, fragrant resinous material obtained from artificially-made in-

cisions in the trunk of *Myroxylon toluifera*, a tree indigenous to New Granada. When in the fresh condition it is a soft, tenacious mass, which becomes harder on keeping, and is in cold weather quite brittle. A fragment warmed and pressed on to a microscopic slide by the cover glass exhibits crystals of cinnamic acid under the microscope.

It contains the benzoic and cinnamic esters of benzyl alcohol, free cinnamic and benzoic acids, traces of vanillin, and esters of a complex alcohol which has been named toluresinotannol. A very small amount of an essential oil is also present.

Balsam of tolu is adulterated, either by the addition of other resinous matter, or by the abstraction of some of its odorous constituents. A pure balsam should yield not less than 90-98 per cent. of soluble matter to 90 per cent. alcohol, and under 10 per cent. to petroleum spirit.

A pure balsam should yield a distinctly crystalline residue to carbon bisulphide. This residue should weigh at least 25 per cent. of the weight of the sample.

Common rosin may be detected by exhausting 5 grams with petroleum ether and shaking the filtered solution with an equal volume of a 0.1 per cent. solution of acetate of copper. In the presence of colophony the petroleum ether will be coloured a brilliant green, due to the soluble copper salt of abietic acid.

A genuine balsam of tolu should have an acid value from 92 to 135, and an ester value of 59 to 91.

Delphin (*Svensk. Pharm. Tidskr.*, 1907, 3, 415) recommends the following method of analysis. Two grams are dissolved in 25 c.c. of ether, and normal solution of KOH is added. After shaking, the aqueous liquid is run into a flask, the ether washed with a little water, and the wash water added to the original aqueous liquid. The ethereal solution is evaporated on a water bath and exposed over sulphuric acid in a desiccator for eighteen hours, and weighed. This gives the cinnamein, which should be not less than 8 per cent. The alkaline liquid is treated with sodium bicarbonate until an abundant precipitate is formed, and a current of CO<sub>2</sub> is run through the liquid for an hour. The solution is filtered, and the precipitate washed with warm water to remove alkali. This precipitate is dried to constant weight, and gives the resin esters. The filtrate from the resin esters is treated with 6 to 7 c.c. of hydrochloric acid, and the resin acids collected on a tared filter, washed with water, dried and weighed. The weight should not exceed 1 per cent. The filtrate is extracted with ether

and the ethereal extract titrated with decinormal potash, with phenolphthalein as indicator. One cubic centimetre of  $\frac{N}{10}$  alkali corresponds with 0.0148 gram of cinnamic acid, which should be present to the extent of 25 per cent. at least.

According to Cocking and Kettle (see *P. & E. O. R.*, 1918, 202), the method of the British Pharmacopœia, 1914, for the estimation of the balsamic acids in balsam of tolu is unsatisfactory, as much of the aromatic acid present is combined with resin alcohols and is insoluble in, and thus not extracted by, carbon disulphide.

In 1914 the authors described a process for the evaluation of benzoin by which the balsamic acids could be separated from the resinous matter, and the free and combined benzoic and cinnamic acids determined (*Year Book of Pharmacy*, 1914, p. 355), and this process is now modified to meet the case of tolu balsam. Boiling out of the aromatic acids with magnesium oxide and water, in the presence of a small quantity of xylene to soften the resinous matter, was found to be the most satisfactory way of dealing with the balsam. The magnesium salts of the aromatic acids are readily soluble in cold water, those of the resin acids being insoluble. A complete separation is effected, and the aromatic acids are obtained in a purer condition than by aqueous extraction alone.

The mode of procedure is as follows :—

(1) *Free Balsamic Acids*.—Five grams of the balsam are dissolved in 25 c.c. of hot alcohol in a 250 c.c. CO<sub>2</sub> flask, 5 grams of light magnesium oxide and 20 c.c. of xylene are added, and the flask shaken round until the contents are well mixed. One hundred cubic centimetres of water are now added, the flask connected to a reflux condenser, and boiled for one hour. After cooling, the whole is poured on a Buchner filter, and the aqueous portion of the filtrate separated from the xylene layer, which is returned to the flask together with the filter paper and adhering magnesia-balsam magma. A second 100 c.c. of water is added and the flask again boiled for an hour, when the aqueous portion is separated as before and the extraction carried out a third time. The bulked aqueous liquids are washed once with 20 c.c. of ether, then rendered acid with hydrochloric acid, and the precipitated acids extracted by shaking out with ether. The greater part of the ether is distilled off, and the residual aromatic acids dried *in vacuo* over sulphuric acid, and weighed.

(2) *Total Balsamic Acids*.—2.5 grams of the balsam are saponi-

fied by boiling with excess of alcoholic potash ; most of the alcohol is then evaporated off, the residue dissolved in 100 c.c. of hot water, and sufficient hydrochloric acid added to render the whole slightly acid. Five grams of light magnesium oxide and 20 c.c. of xylene are next added, and the whole boiled up under a reflux condenser for one hour. The aqueous liquid is separated, the extraction twice repeated, and the bulked aqueous liquids treated as in the case of the free balsamic acids.

The proportion of cinnamic acid is determined by the gain in weight on bromination, details of which may be found in the previous note (*Year Book of Pharmacy*, 1914, p. 355).

The aromatic acids obtained from balsam of tolu are not quite

No.	Acid Value.	Ester Value.	Saponification Value.	Per cent. Free Benzoic Acid.	Per cent. Free Cinnamic Acid.	Per cent. Combined Benzoic Acid.	Per cent. Combined Cinnamic Acid.	Per cent. Total Balsamic Acids.
1	111.8	71.2	183	8.55	11.99	6.19	5.93	32.66
2	112.3	79.0	191.3	9.12	11.53	7.87	6.56	35.08
3	98.1	79.1	177.2	8.48	11.86	8.35	8.68	37.37
4	100.6	72.2	172.8	7.8	10.69	7.45	8.92	34.86
5	118.2	60.8	179	9.1	13.7	5.94	8.97	37.71
6	92.2	62.6	154.8	6.63	12.4	6.17	8.67	33.87
7	101.3	65.9	167.2	8.29	13.71	5.37	10.13	37.5
8	102.5	59.3	163.8	8.34	13.54	5.22	9.08	36.18
9	96.6	65.0	161.6	7.86	13.12	6.43	9.95	37.36
10	132.4	66.2	198.6	7.42	15.9	11.1	5.2	39.86
11	140.1	39.4	179.5	—	—	—	—	24.74
12	124.3	58.3	182.6	—	—	—	—	24.4
13	117.8	90.9	208.7	—	—	—	—	47.56
14	108.9	85.3	194.2	—	—	—	—	45.12

so pure as those from benzoin. The brominated acids from tolu are slightly brown in colour, and contain a substance which is extremely pungent and lachrymatory.

Balsam of tolu, as a rule, contains very little that is not soluble in alcohol, but occasionally samples are met with containing woody matter. Three such samples contained 1.6, 8.9, and 9 per cent. of insoluble matter.

Moisture, generally present, was estimated by spreading in a thin layer on a sheet of glass and drying *in vacuo* over sulphuric acid. Amounts varying from 2 to 8.6 per cent. were found, and the dried balsam was usually quite brittle.

The determination of the acid value of the balsam is somewhat

difficult, owing to the dark colour and to the precipitate which is formed on running in the alcoholic potash. We find it best to proceed as follows :—

Dissolve 5 grams of the balsam in about 50 c.c. of boiling alcohol, add a large quantity of phenolphthalein solution—3 or 4 c.c.—titrate the hot solution with normal alcoholic potash until the colour becomes dark brown (but not red), then attach to a reflux condenser, boil up for a few minutes in order to break up the precipitate, and finish the titration.

By this method titrations agree to about  $0.2 \text{ c.c. } \frac{N}{1} \text{ KOH.}$

The variations from a large number of samples of balsam examined during the last few years are shown in the table on p. 70.

Excluding numbers 11 and 12, which, from their low content of balsamic acids, are probably sophisticated, the figures indicate a range of—

92.2 to 132.4 for acid value,

59.3 to 90.9 for ester value,

154.8 to 208.7 for saponification value,

and 32.68 to 47.50 per cent. of total balsamic acids.

The pharmacopœial limits for acid value are from 107.4 to 147.2, and for saponification value 170 to 202.

Judged by these figures, numbers 3, 4, 6, 7, 8, and 9 would be rejected for low acid values; also the saponification values of numbers 6, 7, 8, 9, and 13 lie outside the limits, although the poorest of these balsams contains 33.87 per cent. of balsamic acids. On the other hand, numbers 11 and 12, though abnormally low in balsamic acids, would be admitted as genuine.

**BANDOLINE.**—A name given by French perfumers to substances used to keep the hair fixed when it has a tendency to “straggle.” They are usually perfumed mucilages, preferably of gum tragacanth, but sometimes of gum arabic or quince mucilage. As they are liable to decompose, a little salicylic or boric acid is usually added to preserve them.

**BARIUM SULPHATE.**—This substance, known as barytes, and also as “*blanc fixe*,”  $\text{BaSO}_4$ , is used to a small extent in some of the cheaper types of face powders or enamels. It occurs naturally as a mineral, but as it must be in an exceedingly fine state of subdivision for use in the perfumery industry, the natural substance is not so suitable as an artificially precipitated sulphate,

which is obtained as an impalpable powder. One of the most suitable forms of this article so far as this point is concerned is the by-product obtained in the manufacture of hydrogen peroxide.

**BAROSMA VENUSTA, OIL OF.**—From the leaves of *Barosma venusta* Gouilding and Roberts (*Jour. Chem. Soc.*, 105, 2613) obtained 2 per cent. of an essential oil having an agreeable aromatic odour. It contains myrcene, estragol, linalol, aldehydes, sesquiterpenes, and a small quantity of esters and phenols. It has the following characters :—

Specific gravity	0.865
Optical rotation	+ 0° 47'
Acid value	5.6
Saponification value	6.2
Saponification value (after acetylation)	55

**BASIL, OIL OF.**—Sweet basil oil is distilled from the entire fresh plant *Ocimum basilicum*. It is a plant of the N.O. *Labiatae*, growing in Europe, northern Africa, Réunion, Java, and Algeria, etc. The oil is of a fragrant odour, and is of use in the preparation of perfumes of the types of violet, mignonette and jonquil, etc.

There are several varieties of the plant, which has been very completely investigated by E. G. and C. Camus (*Roure-Bertrand Fils, Bulletin*, October, 1910, 23). Of these the most suitable for cultivation is the variety *Crispum*. The following are representative characters of the oils from the principal varieties :—

	Specific gravity.	Rotation.	Refractive index.
<i>Thyrsiflorum</i>	0.916	— 11°	1.488
<i>Crispum</i>	0.912	— 10°	1.484
<i>Album</i>	0.898	— 13°	1.479
<i>Purpurascens</i>	0.896	— 14°	1.477

A normal oil distilled in Europe (French or German) has a specific gravity 0.900 to 0.930 ; optical rotation, — 6° to — 20° ; refractive index, 1.4800 to 1.4950 ; and ester value, up to 12. Basil oil from Mayotte has a specific gravity 0.960 to 0.967, and optical rotation about + 1°. Basil oil from Java has been obtained by distilling the large-leaved variety, which is known locally as *Selasih mekah*. It contained about 30 to 40 per cent. of eugenol. A sample distilled in the Seychelles (*Bull. Imp. Inst.*, xvi., I., 30) had a specific gravity 0.962 ; optical rotation, + 0° 50' ; refractive



index, 1.5140; and ester number, 2.5. The European distilled oil contains methyl-chavicol (estragol), linalol, cineol, pinene, and camphor. Besides the above, several other species of basil yield fragrant essential oils, of which the following are the principal:—

*Ocimum canum* is a native of Madagascar, East Indies, China, and Brazil. A sample of the oil distilled from material grown at Dakalba (Ivory Coast) has been examined by Roure-Bertrand Fils (*Bulletin*, October, 1913, 18). It is an oil of pleasant odour, and is semisolid at ordinary temperatures. It has the following characters: specific gravity at 32°, 1.033; optical rotation,  $-2^{\circ} 30'$ ; and saponification value, 301. Its chief constituent is methyl cinnamate, which causes the crystallisation of the oil. *Ocimum gratissimum* is a native of Bengal, Chittagong, Nepal, and the Deccan. It is a plant whose leaves have a remarkably pleasant lemon odour. It is found in native gardens and round about the temples of the natives. It is found also on the Ivory Coast, and a sample distilled at Dakalba, and examined by Roure-Bertrand Fils (*loc. cit.*), was found to have a specific gravity 0.910, and optical rotation  $+1^{\circ}$ . It contains thymol and carvacrol. A sample distilled in the Seychelles (*Bull. Imp. Inst.*, xvi., 1, 30) had a specific gravity 0.995; optical rotation,  $-14^{\circ}$ ; and refractive index, 1.5260. A sample of the oil from this species has also been reported on by the Imperial Institute (*Bulletin*, vol. xxii., 3, 1924), and found to have the following characters:—

Specific gravity . . . . .	0.996
Optical rotation . . . . .	$-12.7^{\circ}$
Refractive index . . . . .	1.5320
Phenols . . . . .	55 per cent.

and, according to Roberts (*Jour. Soc. Chem. Ind.*, 1921, 40, 164, T.), had the following composition:—

Terpenes, principally ocimene . . . . .	16.0 per cent.
Phenols (eugenol) . . . . .	55.0
Phenol ethers (as methyl-chavicol) . . . . .	5.6
Alcohols (linalol ?) . . . . .	13.0
Esters as linalyl acetate . . . . .	0.6
Undetermined . . . . .	9.8

The fruits of *Ocimum Americanum*, from South Africa, were distilled, and the oil examined at the Imperial Institute (*Bulletin*, vol. xxii., 3, 1924). It had a specific gravity 0.953; optical rotation,  $+2.75^{\circ}$ ; and refractive index, 1.5110 at 24°.

Goulding and Pelly (*Bull. Imp. Inst.*, 1908, vi., 209) have examined the oil from *Ocimum viride*, distilled in Sierra Leone. It had a specific gravity 0.911, and optical rotation  $+1^{\circ} 30'$ .

It contained from 32 to 65 per cent. of thymol, 30 to 40 per cent. of alcohols, and a small amount of esters and terpenes.

Glichitch (*Bull. Soc. Chim.*, 1923, iv., 33, 1536) reports on two oils from *Ocimum viride*, one distilled in Grasse, and the other in New Caledonia. The Grasse oil, which was obtained to the extent of 2.588 per cent., was a golden-yellow oil having an odour of thymol. It had a specific gravity 0.9104; refractive index, 1.4962 at 22°; optical rotation, + 0.9°; esters, 1.96 per cent.; total alcohols, 32.53 per cent.; and phenols, 38 per cent.

The oil from New Caledonia had a specific gravity 0.9235 at 25.5°; refractive index, 1.4945 at 22°; optical rotation, + 1.5°; esters, 0.73 per cent.; total alcohols, 26.34 per cent.; and phenols, 18 per cent.

*Roure-Bertrand Fils* (*Bulletin*, October, 1912, 71) have examined two samples of oil of basil from Mayotte. The odour of these oils was good; it recalls, besides that of estragol, a somewhat distinct odour of anethol. They appear to have been prepared under favourable conditions. The first of these samples was of brownish colour; the second was almost colourless.

Their characters were as follow:—

	1	2
Specific gravity at 15° C. .	0.9677	0.9630
Optical rotation . . .	+ 0° 58'	+ 0° 56'
Solubility in 80 per cent. alcohol . . . . .	3 vols. and over.	3.2 vols. and over.
Acid value . . . . .	1.4	0.7
Saponification value . .	5.6	6.3
Esters (as linalyl acetate) .	1.9 per cent.	2.2 per cent.

These oils differ from the oils of basil of Grasse or Bourbon in their *dextro*-rotation and their high specific gravity.

The so-called holy basil is *Ocimum sanctum*. It is common in India, where it is known as *Tulsi* or *Tulasi*. It is venerated by the Hindus, as the vervain was amongst the Romans. The worship of the plant is expounded in a book entitled "*Tulaskiavaçam*," which contains a hymn in honour of the plant. The oil from the leaves has been examined by Bacon (*Philippine Journal of Science*, 1910, 5, 261), and found to have a specific gravity 0.952 at 30°, and refractive index 1.5070. It contains methyl-chavicol, cineol, and linalol. *Ocimum pilosum* is an Indian plant known as *Babooi-*

*tulsi* in Bengal and the neighbourhood. Bhaduri (*Jour. Amer. Chem. Soc.*, 1914, **36**, 1772) has examined the oil distilled from the whole herb. It is a pale yellow oil containing limonene, citral, citronellal, cineol, and thymol, but no methyl-chavicol. Its specific gravity is 0.887 at 25°; optical rotation, — 3.7°; and refractive index, 1.4840 at 25°.

*Ocimum minimum*, the dwarf basil, yields an oil containing about 14 per cent. of eugenol, and probably linalol. Its specific gravity is from 0.890 to 0.910; optical rotation, — 11° to — 14°; and ester value about 12.

**BATH SALTS.**—Bath salts, or bath crystals, are practically invariably composed of sodium carbonate, with, occasionally, the addition of a little borax. The use of bath salts does, in fact, soften hard water in which much lime exists, but they are actually used rather as an attractive vehicle for perfume in the bath. Sodium carbonate,  $\text{Na}_2\text{CO}_3 + 10\text{H}_2\text{O}$ , in crystals of size according to taste, is the base of nearly all bath salts, the fine crystalline so-called sodium sesquicarbonate being rarely obtainable to-day. They are usually tinted with a coal-tar colour, generally basic colours, which are sprayed in solution on the crystals, or the carbonate may be immersed in an alcoholic solution of the dye, drained, and dried. In perfuming the crystals, perfumes should be chosen which are not affected by alkalies, as otherwise a more or less speedy decomposition of the perfume will take place. As sodium carbonate is liable to effloresce, a little glycerine is often added to the crystals to counteract this tendency. Bath powders and water softeners are usually merely powdered dried sodium carbonate, with or without a little borax, coloured and perfumed to taste. A little perborate of sodium is sometimes added.

**BATTEUSE.**—This is the name given to a machine, in France, used for beating up a pomade or concrete with alcohol to prepare an alcoholic solution of their odorous substances, either for a finished product such as a “triple extract,” or for further conversion into an “absolute.”

**BAY, OIL OF.**—Bay leaves, from which the West Indian bay oil is distilled, are, principally, the leaves of *Pimenta acris* (*Myrcia acris*), but no doubt other closely allied species are from time to time mixed with them. The tree is a handsome one, growing to the height of 20 to 40 feet, of pyramidal form. In the woods of Antigua, Jamaica, and Barbadoes the fragrance of these

trees permeates the atmosphere, so powerful is the odour of the essential oil contained in the leaves. The leaves yield from 1 to 1.5 per cent. of essential oil, which contains constituents of such different specific gravities that the oil is often collected in light and heavy fractions in such an erratic manner that the commercial oil is frequently nothing more than a fractionated oil of varying richness in phenols—the characteristic odour bearers of the oil. This has caused a determined effort on the part of the authorities to place the industry on a sound basis, and to ensure the manufacture of an oil of comparatively constant composition. These experiments commenced in 1908, and Sir Francis Watts, the Commissioner of Agriculture for the West Indies, states that the results obtained from the experimental plot then established showed that the cultivation of the tree was a matter worthy of the attention of inhabitants of the islands having uncultivated land at their disposal. Trees were planted in 1908, and distillation commenced in 1911, the leaves yielding practically 1 per cent. of oil. By 1913 the actual yield of leaves had nearly doubled, and these also yielded a higher percentage of essential oil. He also states that experiments in Montserrat and Antigua show that the specific gravity and phenol content of the essential oil are influenced considerably by the character of the leaves collected for distillation, especially as the use of immature leaves lessens the amount and value of the oil.

Assuming that the distillation has been carried on satisfactorily and the whole of the oil obtained has been bulked, a normal West Indian bay oil has the following characters : specific gravity, 0.965 to 0.985 ; optical rotation,  $-0^{\circ} 30'$  to  $-4^{\circ}$  ; refractive index, 1.5100 to 1.5250 ; and phenol content from 55 to 70 per cent. But if the oil is not so distilled, very different results will be obtained. To indicate the differences so obtainable, 150 lb. of leaves were distilled in the Government laboratory at Antigua, and the oil coming over at intervals of about an hour each was examined, with the following results :—

Hours.	Specific gravity.	Phenol content. Per cent.
1 . . . . .	0.8669	.. 23
2 . . . . .	0.9241	.. 78
3 . . . . .	1.0259	.. 89
4 . . . . .	1.0381	.. 93
5 . . . . .	1.0409	.. 95
6 . . . . .	1.0432	.. 96
7½ . . . . .	1.0434	.. 99
9 . . . . .	1.0436	.. 96

The oil obtained in the first hour amounted to nearly half of the whole quantity.

The unsatisfactory variations in the commercial oil, which have not yet disappeared, are explained in the account given by Professor Markoe (*Pharm. Jour.*, [3] viii., 1005), who thus describes the process: "The apparatus used in distilling the oil was a 200-gallon copper still heated by steam, so arranged that either wet or dry steam could be used at pleasure. From 200 to 300 lb. of leaves were used at each running of the still, and to work off this quantity required from eight to twelve hours, during which time from 80 to 100 gallons of distillate would be obtained. The oil comes over in two portions. First, a portion lighter than water, that comes over very rapidly, and then the heavy oil, that comes over very slowly and does not easily separate from the water, with which it forms a milky emulsion. The following notes were made of one of the runs with 200 lb. of leaves. The distillate was collected in quantities of  $2\frac{1}{2}$  gallons of the water carefully separated from each portion. The light oil came over in the first 15 gallons of distillate, from which it promptly separated, leaving the water quite clear. The specific gravity of each of the six portions was as follows: 0.870, 0.930, 0.946, 0.964, 0.982, 0.990. The distillation was then continued to obtain the heavy oil until 65 gallons more of distillate were obtained. This oil was received in three portions, and the specific gravity of each portion then taken: 1.023, 1.035 and 1.037."

An oil of bay distilled in Fiji has been examined at the Imperial Institute and found to contain only 23 per cent. of phenols, in spite of a specific gravity 0.961, but to be very rich in phenol methyl-ethers.

Oil of bay contains pinene, and probably dipentene, together with its principal constituent, eugenol, and its methyl ether. Chavicol, methyl-chavicol and citral are also present. Power and Kleber do not agree that pinene and dipentene are present, but consider the only terpene in the oil to be phellandrene. These chemists also detected a small quantity of the olefinic terpene, myrcene, in the oil.

The odour of the oil is typically phenolic, but differs from that of oil of cloves or oil of pimento on account of the presence of its subsidiary constituents.

West Indian bay oil forms the basic perfume for bay rum (*q.v.*).

The Californian bay is an entirely different tree from that described above. It is *Umbellularia Californica*, often known as

the mountain laurel or the Californian olive. This tree has highly odorous leaves, which yield an essential oil which, according to Power and Lees, contains as its principal constituent a ketone,  $C_{10}H_{14}O$ , which they have named umbellulone. The oil contains a small quantity of eugenol, 20 per cent. of cineol, and 10 per cent. of eugenol methyl ether. It has a specific gravity 0.950, optical rotation  $-36^{\circ}$ , and refractive index 1.4833.

**BAYBERRY.**—The bayberry, candleberry, or wax myrtle of Northern America is *Myrica cerifera*, a branching shrub of 4 to 8 feet in height. It yields a fragrant essential oil having a specific gravity about 0.917, optical rotation  $-1^{\circ} 30'$ , and refractive index 1.4990. It resembles the oil from the leaves of the bog myrtle (*q.v.*). The berries also yield a wax of considerable value, and practically identical with bog myrtle wax. It burns in candle form, with a very white flame with very little smoke, and gives off a very agreeable odour. There are several allied species of *Myrica* indigenous to South Africa, which yield a myrtle wax.

**BAY RUM.**—Bay rum is a very highly esteemed toilet preparation, used in general as a hair wash or as a lotion sprayed on the face after shaving. The preparation was originally sent from the West Indies to this country, and this imported article was highly esteemed. It is probable that it was originally a distillate of rum with the bay leaves, but later a mixture of bay, pimento and cloves was used. To-day very little bay rum is imported, as every perfumer manufactures his own according to his own private formula. The use of rum as the solvent has now almost entirely disappeared, and the best bay rum is now made from alcohol and the various essential oils containing eugenol, bay oil, of course, predominating. Terpeneless oils have been recommended for this purpose, and may effect a slight economy in alcohol, but as most of the oils concerned—bay, pimento, cloves, and cinnamon leaf—are very rich in phenols, the use of the terpeneless oils is probably more expensive than filtering off the small quantity of insoluble constituents.

Cheap bay rum is made with methylated spirit, further denatured by the addition of extract of quassia. This must not be done, however, without the permission of the Customs authorities. A suggestion of the presence of rum is sometimes given by the addition of an artificial essence of rum. This is, in its best varieties, a mixture based on an impure ethyl acetate made from crude pyroligneous acid.

**BDELLIUM** is a somewhat aromatic resin which has a resemblance to myrrh, and is often found in admixture with it. It occurs as African bdellium and East Indian bdellium. It is the product of various species of *Commiphora* and *Balsamodendron*. It can be distinguished from myrrh by its not yielding the characteristic reaction with nitric acid. This reaction is as follows. The gum resin is extracted with ether and the ether evaporated. The residue is brought into contact with the fumes of nitric acid. Genuine myrrh gives a violet colour, which is not the case with bdellium.

Bdellium contains about 75 per cent. of resin soluble in alcohol. The following figures for bdellium are due to Dieterich :—

	Acid value.	Ester value.
African . . . . .	12.8	70
„ . . . . .	14.4	69.3
„ . . . . .	9.7	96.4
„ . . . . .	11.9	95.6
„ . . . . .	19.2	90.7
„ . . . . .	20.8	90.1
Indian . . . . .	35.7	46.8
„ . . . . .	37.2	48.5

(See also under “Incense.”)

**BEESWAX.**—Beeswax is used by the perfumer in the manufacture of cold creams and similar preparations. Natural or yellow beeswax, the *Cera flava* of pharmacy, is the substance secreted by the hive bee, *Apis mellifica*, and probably other species, to build up the skeleton of the honeycomb. After the honey has been extracted, the wax is melted with water, separated, and strained. Beeswax varies from pale yellow to deep brown in colour, this feature depending largely on the food of the bees. It is hard, solid, not very unctuous to the touch, and breaks with a dull granular fracture. It has an agreeable honey-like odour.

The natural beeswax is bleached to a clean white colour, either by exposing it in thin layers to the action of air, moisture and sunlight, or by treating it with chemicals such as dilute chromic acid. Chemically-bleached beeswax is more brittle than air-bleached wax, and retains traces of acid, which renders it rather less desirable for perfumery purposes than the air-bleached variety. Pure beeswax should have the following characters: specific gravity at 15°, from 0.958 to 0.968; melting point, 61° to 64°; refractive index at 80°, from 1.4380 to 1.4420; acid value, 16.5 to 22.5; ester value, 68 to 78; and saponification value, 85 to

100. Chemically-bleached wax may have a slightly higher acid value than that given above.

The principal adulterant of beeswax is ceresine or paraffin wax, which are far less expensive. Sometimes stearic acid and carnauba wax are used as adulterants, though this is but rarely the case to-day.

**BELLARY LEAF OIL.**—The leaves of *Litsea zeylanica* yield about 0.6 per cent. of an odorous essential oil of specific gravity 0.890; optical rotation,  $+1.5^\circ$ ; and ester value, 15. It is an Indian essential oil, which has not, so far, been produced on a commercial scale for perfumery purposes. It probably contains geraniol (*P. & E. O. R.*, 1923, 14, 271).

**BENZALDEHYDE.**—Benzaldehyde,  $C_6H_5.CO.H$ , is the essential principle of the oils of almond, peach and apricot kernels. These oils contain little else but benzaldehyde, so that the artificially prepared substance is very commonly used in place of the natural essential oils. It is a highly refractive liquid, of specific gravity 1.052; refractive index, 1.5450; and boiling point,  $180^\circ$ . It rapidly oxidises to benzoic acid, so that it should be kept from exposure to air and moisture. The usual starting point in the manufacture of benzaldehyde is the coal-tar hydrocarbon, toluene, which must be separated from accompanying impurities before it can be used for this purpose. It is heated, preferably in a brilliant sunlight, to boiling point, and a current of chlorine gas is passed through it until it has absorbed 40 per cent. of its weight. The benzal chloride  $C_6H_5.CH.Cl_2$  so formed is mixed with three times its weight of water and its own weight of powdered chalk, and the mixture heated for four hours to  $130^\circ C$ . The mixture is then steam-distilled and the crude benzaldehyde purified by conversion into its crystalline bisulphite compound (see "Aldehydes, Determination of"), which is rendered alkaline, and the liberated benzaldehyde steam-distilled.

Benzaldehyde so manufactured is invariably contaminated with organic chlorine substitution products. This fact renders it of little value if used for perfuming pale-coloured substances such as white soap, as products perfumed with it steadily darken in colour. Hence it becomes necessary either to eliminate such chlorine compounds or to manufacture a benzaldehyde free from chlorine by a process in which no chlorine is used. The following are examples of such methods. Three hundred kilograms of toluene are mixed with 700 kg. of 65 per cent. sulphuric acid and



well agitated, with the gradual addition of 90 kg. of finely powdered manganese dioxide, keeping the temperature at about 40°. Or 300 kg. of toluene are mixed with 150 kg. of oxide of nickel and heated to 100° for six hours, by which a direct oxidation of the toluene takes place.

Chlorine-free benzaldehyde is used as an adulterant of essential oil of almonds, but as most samples of the so-called chlorine-free substance contain *minute* quantities of chlorine (which is not harmful for any perfumery purpose), the detection of these traces of chlorine becomes important, as there is a considerable divergence between the prices of the natural and the artificial products. The following simple method will detect chlorine when present in appreciable amount. A piece of filter paper about 2 inches by 1 inch is rolled in the shape of a spill and saturated with the liquid. The paper is placed in a small porcelain dish, which stands in a larger dish, so that a glass beaker can be inverted over the smaller dish whilst resting in the larger one. The paper is set alight and the beaker, moistened with distilled water, inverted over it. When the flame is extinguished, the inside of the beaker is rinsed out with distilled water into the outer dish, the liquid, filtered and tested with silver nitrate for chlorides. A turbidity or precipitate indicates the presence of an appreciable amount of chlorine. For the detection of very minute quantities Salamon recommends the following process. About 2 grams of the benzaldehyde are heated in a retort with 40 c.c. of concentrated sulphuric acid, and 5 c.c. of nitric acid in a small retort, and the fumes collected in a solution of silver nitrate until no further precipitate is obtained. The liquid is heated with dilute nitric acid, and the precipitated silver chloride separated and weighed. This method will detect as little as 0.01 per cent. of chlorine. Voigt (*Z. Angew. Chem.*, 1922, 35, 654) has described a combustion method which is tedious, but gives accurate results.

**BENZOIC ACID.**—This acid,  $C_6H_5.COOH$ , is the simplest acid of the aromatic series. It is found to a small extent in the free condition, but principally in the form of esters (*vide* "Benzoin"). It is a crystalline substance melting at 121°, and having a slightly aromatic odour suggestive of vanilla. To obtain it from benzoin the dry powdered gum is placed in a metal receptacle, covered with a filter paper pierced with pin holes, and covered with a paper hood. The powder is heated, and the benzoic acid sublimes and collects on the paper hood. It is prepared on a considerable scale artificially by the hydrolysis of the chlorination

product of toluene. It is employed largely as a preservative of fats, such as lard, etc.

**BENZOIN.**—Benzoin, or Gum Benjamin, as it is often called, is an important balsamic resinous material, much used in the perfumery industry, both on account of its sweet heavy odour and its useful fixative properties. It is used in the manufacture of incense. The earliest literature dealing with the subject speaks of benzoin as *Luban Jawi* ("incense of Java"), the name Java being used for Sumatra and other neighbouring islands. It is easy to trace the modern name through successive corruptions of the above name: banjawi, benjui, benzoi, benzoin, and benjamin. There are several types of benzoin, of which Siam benzoin is preferred for perfumery purposes. This is the product of a tree not yet identified with certainty, but which may be *Styrax Tonkinense*. The trees do not produce the secretion normally; a wound is inflicted in the bark sufficiently deep to injure the cambium, which results in the formation of oleoresin ducts in which the secretion is produced. It is, in fact, a pathological secretion. When sufficiently hard and dry, the material is collected, either in the form of lumps or in small tears. The principal constituents of Siam benzoin are free benzoic acid and the benzoic ester of the alcohol lubanol. There are also present siaresinyl benzoate, vanillin, and traces of other aromatic substances. The combined benzoic acid amounts to about 25 per cent., and the free benzoic acid to about 15 per cent. It should yield 90 per cent. at least of extract to alcohol, and should not contain more than 2 per cent. of mineral matter.

Reinitzer (*Arch. Pharm.*, 1921, 259, 1, 60) has isolated a small amount of siaresinolic acid from Siam benzoin. It is a crystalline substance of the formula  $C_{30}H_{48}O_4$ , melting at  $260^{\circ}$ . He also fully examined the ester lubanol benzoate,  $C_{17}H_{16}O_4$ , which he found to crystallise in plates melting at  $72^{\circ}$  to  $73^{\circ}$ . For further details the papers above quoted should be consulted.

Sumatra benzoin is of weaker and less agreeable odour than Siam benzoin. It is derived from *Styrax Benzoin*, and owes its odour principally to the cinnamic acid esters of benzoiresinol and benzoiresinotannol. There are also present free benzoic acid, styrol, benzaldehyde, vanillin, phenyl-propyl cinnamate, and styracin.

Other varieties are those known as Palambang, Padang and Penang, but they are not used in perfumery except for the manufacture of incense.

Siam benzoin is esteemed by perfumers on account of its vanilla-like odour. A full and interesting account of the history of benzoin by E. M. Holmes will be found in the *Perfumery and Essential Oil Record*, 1916, 112, in which he gives the following details in regard to Siam benzoin, the method of collection being described in the *Kew Bulletin*, 1895, 195:—

The season for collecting the benzoin is in July or August, when the work in the paddy fields is finished, till November. The trees are notched with an axe, and the exuded soft resin is allowed to remain on the trees for three months to harden, so that the benzoin is ready for sale in December.

It is sorted into three classes. The best, or "Sua," is in large lumps, and is clean; the second consists of smaller lumps, and has some bark attached to it, and is half the value of the first; the third, or "Musi," is soiled with dust and dirt, and is in fine small pieces. It is collected by the Siamese Thai, Annamites, and Tongoos, who have settled in the province and carried on the work from time immemorial. This account is furnished by Siamese, not European, observers.

In 1910 an *apotheker* at Basle, Herr Hartman Rordorf, published an interesting account of the collection and preparation of Siam benzoin in the *Schweizerische Wochenschrift*, having fortunately been able to obtain information through his brother-in-law, Dr. Domeller Nieuwenhuis, the Dutch Minister in Siam, who lived some years in Bangkok. Great difficulty was experienced in obtaining information and specimens. Between 1907 and June, 1910, ten expeditions were sent to obtain material, but all except the last proved unsuccessful. The road and paths in northern Siam are very bad, and the commercial traffic is chiefly carried by the rivers. At high water these are not navigable, and at low water are impassable swamps. The morasses are navigable only for a short period during the year. The period necessary to traverse them is three days before the benzoin-producing region can be reached. In this neglected district there is a settlement of small, long-haired people who collect the benzoin, and who apparently emigrated from China in very early times. They speak an old forgotten language and wear different clothes from the natives of southern Siam.

This method of collecting the benzoin and preparing it for market is as follows: On trunks of 20 to 25 cm. in diameter, pieces of bark of rectangular shape from  $\frac{1}{2}$  to 4 handbreadths in size are loosened, and the resin runs out on the inner side of the bark.

solidifying there by the heat of the sun. This forms the finest quality. The smaller fragments are formed into lumps by hand. The resin is spread out on a strong mat in a heap, and ginger roots, first hollowed and filled with the marrow of the bone of the pig, are mixed with it, and the mats are tied up at the ends into a bundle. The contents are examined from time to time to see if the fat has been taken up, and if not, fresh fat is used. It is said that rancid fat will not, like fresh fat, pass through the ginger root. The process takes about a year, its object being to preserve a fine aroma. When the fat has disappeared from the ginger the drug is ready for export without risk of losing its fine odour through the long hot journey to Bangkok. The natives rub the gum resin with sugar and then make it into an emulsion with water, which is highly prized as a wash and as an addition to baths. The specimen of Siam benzoin in the museum of the Pharmaceutical Society obtained from wholesale commerce in this country bears out this description fairly well. In some specimens large tears of benzoin are attached to the inner surface of a moderately thick bark, and differ from the Sumatra kind not only in the vanilla odour, but in the fact that the tears are unusually free from one another. It seems quite possible that this is due to their having an oily surface, caused by the hog's marrow, which would probably prevent loss of benzoic esters to some extent and thus conserve the natural fragrance of the resin. It is interesting to record that Herr Rordorf has found resin canals to be abundantly present on the inner surface of the bark (*Pharm. Jour.* (4), 31, 515).

The most recent contribution to the knowledge of the tree yielding Siam benzoin was published in 1913 in the *Apotheker Zeitung*, by Dr. C. Hartwich, who received specimens of the mature fruit as well as leaves, bark and resin from Messrs. Bildermeyer and Schoch Billiviller from San Nua, which is nearly in the centre of the Siam benzoin district, between Luang Phrabang and Hanoi.

Dr. Hartwich believes that the produce of this district passes through the town of Luang Prabang into Siam, since Thorel reported in 1866 that the benzoin was collected on the mountains between Laos and Tonkin, in latitude 19 N., in the forests of one of the affluents of the east of the Mekong River on the frontier of Annam. The sample of Siam benzoin received by Dr. Hartwich was white internally and brownish externally, and yielded no cinnamic acid, and the fruits were oval, as might have been

expected from Thorel's herbarium specimens above mentioned. The mature fruits were submitted to the Royal Gardens at Kew for identification, and were there determined by Mr. Craib to be identical with the *Anthostyrax Tonkinense* of Pierre and the *Styrax macrothyrsus* of Perkin.

By the rules of priority, Perkin's name comes first, but as *Anthostyrax* is regarded at Kew as a sub-genus only, Mr. Craib has named the tree *Styrax Tonkinense*. The fruit is elliptical, smooth, with a thin pericarp dehiscing longitudinally into three valves, and an elliptical, oval, dark brown seed, which is rough with minute papillæ. It is thus quite different from the fruit of *S. Benzoin*, which is globular, nearly an inch in diameter, with a thick pericarp, which is indehiscent.

Another species of *Styrax*, *S. benzoides*, Craib, is reported to yield benzoin near Chieng-mai, in Siam, but the resin does not possess the same appearance as the Siam benzoin of commerce, and is probably only used locally. It may therefore be considered proven that *Styrax Tonkinense* is the botanical source of Siam benzoin.

The following are average figures for benzoin of good quality, free from admixture with earthy matter, etc. :—

	Siam.	Sumatra.	Other varieties.
Ash . . . . .	Under 2 per cent.	Under 2 per cent.	Under 3 per cent.
Soluble in 90 per cent. alcohol . .	90-96	90-94	85-95
Acid number . . .	130-158	98-140	106-142
Ester number . . .	42-69	50-100	50-90

Cocking and Kettle, in a paper read before the British Pharmaceutical conference at Chester in 1914, gave the following complete analyses of eleven samples of Sumatra and Siam benzoin (see p. 86).

If Sumatra benzoin be warmed with chromic acid mixture, a strong odour of benzaldehyde is given off, owing to the oxidation of cinnamic acid. This distinguishes it from Siam benzoin. According to Muter, Siam benzoin gives the following characteristic reaction. If the dried petroleum ether extract of the resin is treated with sulphuric acid, a cherry red colour is developed. It is frequently of importance to determine the amount of benzoic acid in benzoin. This can be done by digesting 10 parts of the

# P E R F U M E R Y

No.	Alcohol insoluble.	Moisture.	Dry alcohol soluble.	Acid value.	Ester value.	Saponification value.	Free benzoic acid.	Free cinnamic acid.	Combined benzoic acid.	Combined cinnamic acid.	Total aromatic acids.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1	19.7	14.0	66.3	140.3	64.1	204.4	6.92	9.08	0.98	9.71	26.69
2	24.0	10.6	65.4	139.9	83.2	223.1	6.11	10.73	4.83	6.81	28.48
3	4.3	1.6	94.1	127.0	63.2	190.2	1.12	17.0	1.2	16.62	35.94
4	22.6	10.4	67.0	132.8	65.2	198.0	7.52	8.68	2.14	6.72	25.06
5	21.1	7.0	71.9	137.1	68.4	205.5	6.26	9.76	2.91	8.47	27.4
6	0.5	0.7	98.8	142.4	65.2	207.6	22.34	1.16	12.41	3.32	39.23
7	3.7	1.6	94.7	137.5	65.8	203.3	21.47	2.68	12.2	3.1	39.45
8	20.7	6.0	73.3	142.1	56.5	198.6	8.21	13.21	2.44	4.64	28.5
9	14.6	2.3	83.1	122.9	56.0	178.9	19.33		5.97		25.3
10	21.7	5.6	72.7	122.0	47.0	169.0	18.31		4.4		22.71
11	23.1	5.3	71.6	122.3	81.5	203.8	14.0		7.56		21.56

Nos. 1, 2, 4, 5, 8, 9, 10 and 11 are ordinary commercial samples of Sumatra benzoin.

No. 3 is a particularly fine old sample of Sumatra block. It is very pale in colour, and the aromatic acid present consists almost entirely of cinnamic.

Nos. 6 and 7 are Siam tears and block respectively. The presence of cinnamic acid in these was proved by treating a portion of the mixed acids with potassium dichromate and sulphuric acid, when a faint but unmistakable odour of benzaldehyde was produced.

powdered gum with 6 parts of slaked lime and 100 parts of water. After six hours the liquid is boiled, filtered, and the residue washed. The filtrate is concentrated, acidified with hydrochloric acid, and well cooled. The precipitated benzoic acid is filtered off, washed with a little water, and dried between porous paper. The small amount of benzoic acid left in the mother liquor is extracted with chloroform and dried in a desiccator and weighed. To estimate the total balsamic acids, Cocking and Kettle give the following process: Five grams are extracted with alcohol in a Soxhlet tube and the extract hydrolysed with alcoholic potash. The alcohol is evaporated, the residue dissolved in 100 c.c. of water and rendered faintly acid with hydrochloric acid, and then 5 grams of magnesia and 20 c.c. of xylene added. The whole is boiled under a reflux condenser for an hour, cooled, the aqueous liquid filtered off, and the insoluble matter boiled twice with 100 c.c. of water, which is allowed to cool before being filtered. The combined aqueous extracts are extracted once with ether, then acidified with hydrochloric acid, and the liberated balsamic acids shaken out with ether. The ether is evaporated and the residue dried *in vacuo* over sulphuric acid and weighed.

In the manufacture of incense powdered benzoin always plays an important part (see "Incense"). There is also a plant known as *Benzoin odoriferum* (*Laurus benzoin*), commonly termed spice wood or wild allspice, which grows in various parts of North America. Nearly every part of the plant yields an aromatic oil, that from the bark probably containing cinnamic compounds.

**BENZOPHENONE.**—Benzophenone, or diphenyl ketone  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , is a fragrant crystalline body, melting at  $48^\circ$  and boiling at  $307^\circ$ . Its specific gravity at  $50^\circ$  is 1.098. It is prepared by distilling calcium benzoate or by the condensation of benzene with benzoyl chloride in the presence of aluminium chloride. It is useful in the preparation of heavy odours of the so-called Oriental type.

**BENZOYL ISOEUGENOL.**—This body is a substituted isoeugenol of the formula  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot(\text{C}_9\text{H}_{12}\text{O}_2)$ . It forms small crystals melting at  $59^\circ$ , and has a slight odour. Its principal value, however, lies in its use as a fixative. It is recommended in the fixation of carnation, fern, rose and orchid perfumes.

**BENZYL ACETATE.**—Benzyl acetate is an ester of the formula  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{O}\cdot\text{OC}\cdot\text{CH}_3$ . It occurs naturally in oil of jasmin,

oil of ylang-ylang, oil of tuberose, and similar flower oils. Its odour is sweet, but not intense; it is prepared synthetically, and is indispensable in the preparation of artificial flower oils of the jasmin or ylang-ylang types. It is a colourless oil, soluble in any proportion in 90 per cent. alcohol. Its specific gravity is about 1.060; refractive index, 1.5034; and boiling point, 216°. It may be prepared by boiling for thirty hours a mixture of 5 parts of benzyl chloride, 4 parts of fused sodium acetate, and 4 parts of a glacial acetic acid. Excess of acetic acid is removed by distillation, and the ester is washed and rectified. It should be free from chlorine, as specimens containing more than faint traces tend to discolour soap, etc., which has been perfumed by this substance.

**BENZYL ALCOHOL.**—This body is the lowest member of the normal aromatic alcohols containing the benzene nucleus, It has the formula  $C_6H_5 \cdot CH_2OH$ . It exists in the free state to a small extent in those oils which contain its esters, such as jasmin, tuberose, cassie flowers, ylang-ylang, etc. It is useful in the preparation of such artificial flower oils. It is an oil of specific gravity about 1.048; refractive index, 1.5400; and boiling point, 205° to 207°.

It is useful to the perfumer not only for its slight floral odour, but as a fixative, and also as a solvent for artificial musk.

It may be prepared by mixing magnesium hydrate (1 molecule) with benzyl chloride (2.2 molecules) and adding about ten times the weight of water. The mixture is maintained at 100° for some hours with continual shaking. The yield is about 95 per cent. of the theoretical.

**BENZYL BENZOATE.**—This ester, of the formula  $C_6H_5 \cdot COO \cdot CH_2 \cdot C_6H_5$ , occurs naturally in balsam of Peru, and to a small extent in ylang-ylang, tuberose, and similar flower oils. It is, when quite pure, a crystalline solid melting at 21°. In commerce, however, the artificial ester contains minute quantities of unobjectionable impurities, which keep it liquid at ordinary temperatures, and the melting point seldom exceeds 18° to 19°. It has a specific gravity 1.1224, refractive index 1.5685, and boils at 323°. Its odour is very slight, but strong enough to be of value in reproducing floral odours. It is also a very useful fixative, and an excellent solvent for artificial musk. It should be free from chlorine. It is obtained commercially by dissolving sodium in benzyl alcohol and heating it with benzaldehyde for twenty



four hours on a water bath. The mixture is acidified with acetic acid, and the ester precipitated by water and rectified.

**BENZYL BUTYRATE.**—Benzyl butyrate is an ester which has a softer odour than benzyl acetate, and is indispensable in correcting the harshness of the latter in the best artificial jasmin perfumes. Its formula is  $C_6H_5.CH_2.OOC.(C_3H_7)$ . It has a specific gravity 1.015, refractive index 1.4945, and boils at  $242^\circ$ .

**BENZYL CINNAMATE.**—The cinnamic ester of benzyl alcohol, of the formula  $C_6H_5.CH_2.COO.CH:CH.C_6H_5$ , is found as a natural constituent of storax, balsam of Peru, and balsam of tolu. It is a crystalline substance with a characteristic sweet balsamic odour. It is prepared artificially by heating sodium cinnamate, alcohol and benzyl chloride under a reflux condenser. It forms white crystals melting at about  $32^\circ$ . It boils at  $195^\circ$  to  $200^\circ$ . It is used in the preparation of heavy odours of the Oriental type, and is also useful as a fixative.

**BENZYL CYANIDE.**—This compound,  $C_6H_5.CH_2CN$ , is a natural constituent of oil of neroli and of certain cress oils. It is a liquid of powerful odour, boiling at  $231^\circ$  and having a specific gravity 1.016. It is probably an intermediate substance in the formation of phenyl-acetic acid in plants in which this acid occurs. It is an important intermediate in the preparation of synthetic phenyl-acetic acid, and can be prepared by the action of sodium cyanide on benzyl chloride.

**BENZYL-ETHYL OXIDE.**—This oxide, of the formula  $C_6H_5CH_2.O.C_2H_5$ , is a colourless oil, useful in perfuming soap on account of its resistance to alkalies. It has a penetrating fruity odour.

**BENZYL FORMATE** is an oil having an odour of jasmin. It is somewhat harsh in odour, and should be used in small quantities only. It may be prepared by the action of formic acid on acetic anhydride, and then esterifying benzyl alcohol with the mixed anhydride so formed. Benzyl formate boils at about  $202^\circ$ , and has a specific gravity 1.083, and refractive index 1.5195.

**BENZYL - HEPTINE - CARBONATE.**—*Vide* "Heptine-carbonates."

**BENZYL-METHYL-CARBINOL.**—This body is a fragrant oil, isomeric with phenyl-propyl alcohol. It boils at  $215^\circ$ , and has the formula  $C_6H_5.CH_2.CH(OH).CH_3$ .

**BENZYL PROPIONATE.**—Like the corresponding butyrate, this ester has a softer and sweeter odour than the acetate, and is used to correct the harshness of the latter in artificial jasmin odours. It has the formula  $C_6H_5.CH_2.OOC(C_2H_5)$ . It has a specific gravity about 1.0362; refractive index, 1.4980; and boiling point, 228°.

**BENZYL SUCCINATE.**—This substance, of the formula  $(C_6H_5.CH_2)_2(OOC)_2(CH_2)_2$ , is a crystalline odourless powder melting at 45°. It is a useful fixative.

**BENZYL VALERIANATE.**—This ester, of the formula  $C_6H_5.CH_2.OOC.(C_4H_9)$ , is prepared by esterifying benzyl alcohol with valerianic acid. It has an odour of valerian, and is used in minute quantities in a number of floral oils, such as artificial otto of rose. Its specific gravity is 0.996; refractive index, 1.4880; and boiling point, 250°.

**BENZYLIDENE-ACETONE.**—This ketone,  $C_6H_5.CH:CH.CO.CH_3$ , is of a sweet floral odour. It is used to round off and modify artificial flower oils, but is especially useful as a basic material for artificial sweet pea perfume. It is a crystalline body of specific gravity 1.0377, melting at 42°, and boiling at 260° to 262°. It is prepared by mixing 22.5 kg. of acetone, 15 kg. of water, and 15 kg. of benzaldehyde. The mixture is cooled to 10°, and 9 kg. of 10 per cent. solution of caustic soda is slowly added, with constant stirring, care being taken that the temperature does not rise materially. The excess of acetone is removed by distillation, and acetic acid added. The ketone is then steam distilled. According to Lewinsohn (*P. & E. O. R.*, 1924, 118), a distinct improvement of the yield obtained by these methods results if allowance is made for the fact that water is produced to the extent of 16 per cent. of the benzaldehyde reaction mixture, this water causing dilution of the soda lye. The strength of the 10 per cent. caustic soda solution can be maintained by the gradual addition of a 20 per cent. solution so as to counteract the dilution caused by the water produced in the reaction.

The method of conducting the operation is as follows. In a jacketed mixing vessel of iron—provided with means for heating and cooling by passing steam or water through the jacket—are mixed 22.5 kg. of acetone and 15 kg. of benzaldehyde. The mixture is cooled to about 10°, and 8.7 kg. of 10 per cent. caustic soda solution are slowly added with vigorous stirring. The solution becomes lemon yellow in colour. As a result of the

reaction, 2.54 kg. of water are produced, and, in order to maintain the strength of the solution, ten hourly additions of 250 grams of 20 per cent. caustic soda solution are made, and the mixture is set aside for two days. At the end of this period 20 kg. of cold water are added, thus causing the benzylidene-acetone to precipitate as a brown oil. After washing with dilute acetic acid and sodium carbonate solution, the oil is distilled under diminished pressure, a bright yellow oil coming over at  $151^{\circ}$  to  $153^{\circ}$  under 25 mm. This oil possesses a fresh and characteristic odour, and after a short period, especially if sown with a crystal, the oil solidifies to a bright yellow crystalline solid melting at  $41^{\circ}$  to  $42^{\circ}$  C.

On account of its exceptionally penetrating nature, benzylidene acetone should be used in perfumery with great caution, and only as a 10 per cent. solution in alcohol. Its stability to alkali makes it of special value as a soap perfume. In its concentrated state benzylidene acetone violently attacks the skin. M.D.

**BERGAMIOL.**—This is a name often used for so-called artificial bergamot oil, consisting principally of linalyl acetate made from linalol obtained from linaloc or other oils.

**BERGAMOT OIL.**—This oil is one of exceedingly soft and sweet odour, and is indispensable in the manufacture of many perfumes. It finds a prominent place in all formulæ for eau de Cologne, in many for lavender water, and in a very large number of other fancy perfumes. It is expressed from the peel of the fruit of *Citrus aurantium*, sub-species *Bergamia*, a tree belonging to the natural order *Rutaceæ*. The chief centre of the bergamot industry is southern Calabria, in which district practically the whole of the supply of bergamot oil is produced. There are extensive plantations in the neighbourhoods of Reggio, Melito, Gallico, S. Lorenzo, and other districts. The oil is expressed by machines, distilled oil losing much of its odour and being of little value to the perfumer. The oil varies in colour from a rich golden brown to a distinct green, usually the latter. The green colour is due to the presence of traces of chlorophyll, and not, as is often stated, to copper. The fruits are gathered during November and December, and the oil expressed from the peel and packed in coppers or tins for exportation.

Pure oil of bergamot has the following characters: specific gravity, from 0.880 to 0.887; optical rotation,  $+8^{\circ}$  to  $22^{\circ}$  (rarely, a little higher); and refractive index, 1.4640 to 1.4675. It should yield from 4.5 to 6.5 per cent. of solid residue when dried on a

water bath. This consists of wax, colouring matter, and other substances dissolved by the oil from the peel, including bergaptene (*q.v.*). The principal odorous constituent is linalyl acetate,  $C_{10}H_{17}.CO_2.CH_3$ , which is present to the extent of about 38 to 42 per cent. Oils with much less than 38 per cent. are usually adulterated, the principal adulterant in such cases being lemon terpenes. Such adulterated oils are often fortified with artificial esters to bring up the ester value, in the hope that they will be regarded by the user as natural esters. The presence of many such artificial esters is revealed by the increase in the weight of the non-volatile residue; and by the high saponification value of the latter. The normal residue on the water bath has an acid value about 18 to 30, and an ester value of 115 to 180.

If unripe fruits are used for the preparation of the oil, it may have a specific gravity down to 0.878 or 0.879, and contain less than 30 per cent. of esters.

During the present season (1923-1924) the writer has found undoubtedly authentic samples of bergamot oil having quite abnormal characters. The oils contained only about 35 per cent. of esters, had a low specific gravity—from 0.880 to 0.881—and contained between 6 and 7 per cent. of fixed residue. This fixed residue is normal in character. Ogston and Moore (*P. & E. O. R.*, 1924, 78) have also recorded such samples, which appear to be due to imperfect ripening of the fruits.

There is a bastard bergamot, known as bergamotella (*Nero de Bergamotto*), which is occasionally mixed with the normal fruit. In such cases the specific gravity is raised, as the oil from the bastard fruit often reaches 0.898, and the ester value is reduced considerably.

Bergamot oil contains, besides linalyl acetate, limonene, pinene, camphene, bornylene, bisabolene, *lævo*-linalol, dihydrocumin alcohol, nerol, terpineol, and bergaptene.

**BERGAPTENE.**—This body is the principal constituent of the residue of oil of bergamot when evaporated on a water bath. It is present to the extent of about 5 per cent. It has the formula  $C_{12}H_8O_4$ , and melts at  $188^\circ$ . It is the methyl ether of a phloroglucinol derivative allied to coumarin, and is isomeric with xanthotoxine.

**BETA-IONONE.**—See "Ionone."

**BETA-NAPHTHOL ETHYL ETHER.**—See "Bromelia."

**BETEL, OIL OF.**—The essential oil of *Piper betle* (Chavica betle) is distilled from the leaves of the plant, one of the *Piperaceæ*. The leaves yield up to 1 per cent. of oil (occasionally higher), with a characteristic odour of the plant. It is a heavy, yellowish liquid of specific gravity, usually from 1·020 to 1·050, but sometimes only about 0·960. Its refractive index is over 1·5000. It contains methoxy-chavicol (betel phenol) as its principal constituent, together with a little chavicol, a sesquiterpene, and possibly cineol and cymene. Its odour is persistent and typically phenolic.

**BETEL PHENOL.**—This body is identical with chavibetol, the phenolic constituent of betel oil. (*Vide* “Chavibetol.”)

**BETULA LENTA, OIL OF.**—See “Birch (Sweet), Oil of.”

**BEU-RIENG, OIL OF.**—This essential oil is produced in certain districts of China, and is probably the product of either an *Alpinia* or a *Zingiber* species, but at present its origin is uncertain. It has a very pleasant odour, recalling that of an infusion of tea. Its specific gravity is 0·902; optical rotation,  $-8^{\circ} 8'$ ; and refractive index, 1·4884. It contains over 30 per cent. of free alcohols (Gattefossé, *La Parfumerie Moderne*, 1922, 109).

**BEURRE DE VIOLETTES.**—Owing to its pronounced violet odour, the concrete oil of orris is frequently known under this name.

**BIGARADE.**—This name is applied to the essential oils derived from the bitter orange flowers and fruits, *e.g.*, “oil of orange bigarade” and “oil of neroli bigarade,” in contradistinction to the corresponding oils from the sweet orange, which are known as “oil of orange Portugal” and “oil of neroli Portugal.”

**BIGNONIA.**—*Bignonia suaveolens* (*Sterospermum suaveolens*) is a plant whose flowers possess a most exquisite fragrance, but so far facilities do not appear to have allowed any practical use of them in the perfumery trade. The tree is found throughout the moister parts of India. It is the *Pátalá* of Sanskrit writers, and is known as *Kama-duti* (messenger of love) or *Madhu-duti* (messenger of spring). The flowers are very beautiful in appearance, and of exquisite perfume. Bees prefer them to any other flower, and native poets describe them as the quiver of Kámadéva, the Indian Cupid (Sir W. Jones, “Asiatic Researches,” iv., p. 289).

**BIRCH (SWEET), OIL OF.**—The flavour and perfume of wintergreen are very highly appreciated, especially in the United States. As a perfume material, however, the essential oil of wintergreen is used in this country, not to a great extent for its own odour to predominate, but in small quantities, to modify other and more pronounced odours. But as the essential oil of wintergreen is practically identical with the oil distilled from the bark of *Betula lenta*, the "sweet birch," true oil of wintergreen is to-day seen but little in commerce, as sweet birch oil can be obtained at a much lower price. It should therefore be understood that the expression "oil of wintergreen" is usually meant to indicate that the product is either the distillate of the wintergreen leaves (*Gaultheria procumbens*) or of birch bark (*Betula lenta*), the price indicating whether it be the former or the latter. But it is to be feared that in most cases it is, in fact, the distillate of *Betula lenta*, whatever the price may indicate. Both oils, however, consist almost entirely of the ester methyl salicylate (*q.v.*), so that there is a good deal of fraud in the article, the cheap artificial ester being very frequently substituted for the more expensive natural oil. Apart from price considerations, however, there is practically no difference between oil of wintergreen, oil of sweet birch, and artificial methyl salicylate other than a slight difference in the delicacy of the odour, in regard to which the individual perfumer must make his own decision.

The true wintergreen, *Gaultheria procumbens*, is known also under the names mountain tea, box berry, spice berry, and ground holly. It is a small creeping shrub found in the southern parts of Canada and the northern parts of the United States. All parts of the plant contain essential oil, but the leaves are almost exclusively used for distillation purposes. The apparatus used for distillation is primitive in character, consisting of small whiskey stills or of wooden casks with copper bottoms. The oil does not exist as such in the plant, but in combination as a glucoside, gaultherine, which is decomposed on distillation.

The sweet birch (*Betula lenta*) is a tree which attains a height of 10 to 25 feet, occasionally growing to a height of 75 feet. It is found in moist woods from New England westwards to Illinois, and thence along the Alleghany regions southwards. The best yield of oil is obtained from the wood cut in the summer months. The wood is cut into small pieces and allowed to macerate in water for twelve hours before distillation.

The characters of wintergreen and sweet birch oils are practically

identical. The specific gravity varies from 1.180 to 1.187, and both oils contain from 98.5 to 99.5 per cent. of methyl salicylate. Power and Kleber (*Schimmel's Report*, October, 1895, 50) have made an exhaustive examination of the two oils, and their results indicate that there are only minute differences between the two oils. It is suggested that oil of wintergreen has a very small optical activity—not less than  $-0^{\circ} 25'$ , whilst sweet birch oil is optically inactive. This, however, is very doubtful. A sesquiterpene alcohol, betulol,  $C_{15}H_{24}O$ , and its acetic ester have been identified in sweet birch oil. A test for distinguishing between the two oils has been suggested by J. C. Umney (*P. & E. O. R.*, 1914, 5, 60). To 5 drops of the oil in a test-tube add 5 drops of a 5 per cent. alcoholic solution of vanillin and 1 c.c. of alcohol. Shake well, and add 2 c.c. of concentrated sulphuric acid, and mix thoroughly. Pure wintergreen oil gives an intense crimson-red colour, pure sweet birch oil gives a deep blood-red colour, whilst synthetic methyl salicylate gives a yellow colour.

*Gaultheria punctata*, a plant found in British India and the Dutch Indies, yields an essential oil practically identical with the oils described above.

*Gaultheria fragrantissima* has been experimentally distilled for "wintergreen" oil in Assam, but the yield has, so far, not been sufficient for it to be a commercial success.

If the oil is found to contain traces of chlorine (see under "Benzaldehyde"), it is certain that it is, or contains, artificial methyl salicylate. When of good quality, the artificial ester should contain at least 99 per cent. of true methyl salicylate. It has the following characters: specific gravity, 1.182; optical rotation,  $0^{\circ}$ ; refractive index, 1.5375; and boiling point,  $224^{\circ}$ .

Artificial cassie oil, new-mown hay, and chypre perfumes usually contain very small quantities of methyl salicylate. It is also largely employed as a flavour for chewing gum and for tooth pastes and powders.

**BIRCH TAR OIL.**—This oil is used to dress certain types of leather, originally for the purpose of covering objectionable odour, but to-day rather to impart to the leather the pleasant odour known as that of "Russia leather." It is prepared in Russia by the destructive distillation of the wood and bark of *Betula alba*. The crude tar is redistilled and a brownish oil is obtained, which is known as rectified birch tar oil. It is a liquid of specific gravity from 0.920 to 0.946. It contains over 40 per cent. of phenols, principally guaiacol, creosol, cresol, and xylenol. The crude oil

has a specific gravity 0.928 to 0.960. If a 5 per cent. solution in petroleum ether be shaken with a 0.1 per cent. aqueous solution of copper acetate, it should not become green in colour (absence of fir tar as an adulterant). This oil is known in pharmacy as *Öleum Rusci*.

**BISABOL MYRRH.**—See under “Myrrh” and “Opoponax.”

**BISABOLENE.**—This body is a sesquiterpene,  $C_{15}H_{24}$ , found in the essential oil of bisabol myrrh. It is identical with the hydrocarbon originally discovered in oil of limes by H. E. Burgess, and named by him limene. It is a colourless oil having a specific gravity 0.881; optical rotation,  $-41^{\circ}$ ; refractive index, 1.4901; and boiling at  $112^{\circ}$  at 4 mm. pressure. It has an odour of myrrh.

**BITTER ALMOND OIL.**—See “Almonds, Oil of.”

**BITTER ORANGE OIL.**—See “Orange, Oil of.”

**BLÉ DES PAGODES.**—The essential oil known under this name is of unknown botanical origin. It emanates from Annam, and has been investigated by *Roure-Bertrand Fils* (*Bulletin*, April, 1920, 32). It resembles in odour the oils of palmarosa and ginger-grass, with a definite odour of cummin.

**BLUMEA, OILS OF.**—The oil from *Blumea balsamifera* is an aromatic liquid containing *lævo*-borneol, *lævo*-camphor, a sesquiterpene, a sesquiterpene alcohol, cineol, limonene, and about 5 per cent. of a phenolic compound. It has been examined by Jonas (*Schimmel & Co., Bericht*, April, 1909, 149), who found it to have the following characters:—

Specific gravity	. . .	0.950
Optical rotation	. . .	$-12^{\circ} 30'$
Refractive index	. . .	1.4815
Acid value	. . .	23.4
Ester value	. . .	1
Ester value after acetylation	. . .	198

The phenolic compound is probably phloroglucinol-trimethyl ether.

*Blumea balsamifera* is indigenous to India, and is found from the Himalayas to Singapore, and in the Malay archipelago. It is also found in the islands Hai-nan and Formosa. In Hai-nan and Kwang-tung it is distilled for the production of Ngai camphor, as it is called, or *Ngai-fên*, as the Chinese call it. This substance is used for ritualistic purposes, and also for the manufacture of



so-called "Chinese ink," and in medicine. Ngai camphor is the lævorotatory variety of borneol,  $C_{10}H_{17}OH$  (*q.v.*).

Simonsen and Rau (*Jour. Chem. Soc.*, 1922, 876) have examined the essential oil of *Blumea Malcomii*. This is a small herb, known in Marathi as *Panjrut*. It occurs in the western part of the Deccan plateau at elevations of about 2,000 feet. It has a pleasant camphoraceous odour. The fresh green material yielded about 0.25 per cent. of essential oil, which was found to consist almost entirely of two ketones, *d*-carvotanacetone and *l*-tetrahydrocarvone. Traces of acids, esters, and a phenol were found.

**BOG MYRTLE.**—The bog myrtle (sweet gale, bastard myrtle), *Myrica gale*, has no connection with the true myrtle. It is a native of Britain, and is found in France, Holland, northern Europe, and the United States. It is a small fragrant shrub, found chiefly in boggy places. Its leaves yield a small quantity of a fragrant essential oil having a specific gravity from 0.898 to 0.915; optical rotation,  $-5^{\circ}$  to  $-12^{\circ}$ ; and ester value, 15 to 25. The principal odour value of the plant, however, lies in the fact that the fruit consists of a very large quantity of small berries, which yield, on treatment with hot water, a quantity of wax which, when used for candle manufacture, gives off a delightful odour on burning. Myrtle wax is somewhat variable in colour, usually of a yellowish green shade.

**BOIS DE CITRON.**—See under "Bois de Rose" and "Linaloe Oil."

**BOIS DE ROSE, OIL OF.**—The so-called oil of *Bois de Rose* must not be confounded with oil of rosewood (*q.v.*), which is, as found in commerce, usually an entirely factitious oil. Oil of *Bois de Rose* is frequently known as cayenne linaloe oil, and here again must be distinguished from Mexican linaloe oil, which is the product of various *bursera* species. Cayenne linaloe oil, or oil of *Bois de Rose femelle*, as it is described in full, has usually been described as the product of a tree known as *Licari Kanali*. The botanical origin of the oil has, however, been very obscure until E. M. Holmes published the most reliable account of the matter in 1910 (*P. & E. O. R.*, 1910, 32). The wood, he states, has been named by various writers *Bois de Citron*, *Bois de Rose male*, *Bois de Rose femelle*, *Bois de Cedre jaune*, etc. According to Guibort, the name *Bois de Citron* has been applied to three distinct woods, namely: (1) that of *Amyris balsamifera*, now known to be the tree yielding the West Indian so-called sandal-

wood oil ; (2) an unknown wood of weak odour ; and (3) *Bois de Citron de Cayenne*, also sold as cayenne sassafras wood. This is the wood which yields cayenne linaloe oil. It is the product of a tree for which the native Indian name is *Licari Kanali*, and is known by the French inhabitants as *Bois de Rose male*. The wood known to the French inhabitants as *Bois de Rose femelle* appears to be the product of *Protium altissimum* (*Icica altissima*). This has a lemon-bergamot odour, and differs entirely from *Bois de Rose male*.

So that what is known in Europe as oil of *Bois de Rose femelle* is, in fact, derived from *Bois de Rose male*, the oil from the *Bois de Rose femelle* not being a commercial article at all. Aublet named the tree *Licari guianensis* ("Plantes de Guiane Française," p. 313), but, after fuller investigations, Dr. Moeller showed that there was little doubt that the tree was *Ocotea caudata*. It may be therefore taken for granted that oil of *Bois de Rose femelle*, or cayenne linaloe oil, is the product of the wood of *Ocotea caudata*, known in Guiana as *Bois de Rose male*. The oil obtained by the distillation of the wood is a colourless or pale yellow oil of soft, sweet odour, in which that of its principal constituent, linalol, predominates. It is used for the manufacture of linalyl acetate, the basis of artificial bergamot oil, and as a constituent of such perfumes as lily of the valley, hawthorn, honeysuckle, jonquil, and corylopsis.

The pure essential oil usually has the following characters : specific gravity, from 0.870 to 0.882 ; optical rotation from  $-9^{\circ}$  to  $-18^{\circ}$  ; and refractive index, 1.4600 to 1.4640. It contains only a very small quantity of esters, but from 60 to 80 per cent., sometimes even 90 per cent., of free linalol. It is soluble in 2 volumes of 70 per cent. alcohol. In determining the total alcohols in the oil, as in all oils containing much linalol, special precautions must be taken, or the linalol will be decomposed in the process. To acetylate the oil it should be dissolved in four times its volume of xylene and boiled for about five hours. (*Vide* "Alcohols, Determination of.")

Messrs. Chiris & Co. (*Les Parfums de France*, 1924, 13, 50) have found that many genuine samples of this oil distilled by themselves have specific gravities up to 0.886. They consider that acetylation in xylene solution gives too low results, and that formylation for eighty-four hours in the cold (about  $25^{\circ}$ ) and saponification for ninety minutes give the most accurate determination of the linalol present.

A terpeneless oil of *Bois de Rose* is sometimes offered as being highly concentrated. When it is remembered that the natural oil contains 60 to 90 per cent. of the active constituent, it is obvious that there is not much room for concentration, so that in this case the terpeneless oil possesses but little advantage over the natural oil.

In addition to linalol, the oil contains geraniol, terpineol, cineol, dipentene, traces of furfurol, methyl-heptenone, nerol, and probably isovaleric aldehyde. *Roure-Bertrand Fils (Bulletin, October, 1909, 40)* give the following as the composition of the oil:—

Methyl-heptenone	.	.	.	Traces.
<i>Lævo</i> -linalol	.	.	.	90·5 per cent.
<i>Dextro</i> -terpineol	.	.	.	5·3
Geraniol.	.	.	.	2·4
Nerol	.	.	.	1·2
Other bodies	.	.	.	0·6

**BOKHARA CLOVER.**—This plant, *Melilotus alba*, is a favourite with bees on account of the nectar present in the white clover blossoms. It is one of the contributory causes of the perfume of new-mown hay, a perfume which is to some extent imitated by using coumarin as the basic material.

**BORNEO CAMPHOR.**—This name is the common name for *dextro*-borneol. It is also termed Baros camphor, Malay camphor, and Sumatra camphor. (*Vide* "Borneol.")

**BORNEO CAMPHOR OIL.**—The wood of *Dryobalanops aromatica*, the so-called Borneo camphor tree, yields this odorous essential oil, which contains *dextro*-borneol. It is not often seen in commerce, and is a colourless or pale yellow oil of specific gravity 0·918; optical rotation, +11°; and refractive index, 1·4885. It contains pinene, camphene, *d*-borneol, dipentene, terpineol, and sesquiterpenes.

**BORNEOL.**—Borneol  $C_{10}H_{17}OH$  is the alcohol corresponding to the ketone camphor. It occurs naturally as *dextro*-borneol in *Dryobalanops camphora*, and as *lævo*-borneol in *Blumea balsamifera*. It forms crystalline masses or fine needle-like crystals, which melt at 204° and boil at 212°. Numerous oils of pine needles, derived from *Abies* and *Pinus* species, contain both free borneol and bornyl esters. It is also produced artificially by reducing camphor with sodium. Borneol forms a well-defined series of esters with organic acids of which bornyl acetate is the principal, and which

has a fine pine needle odour. The following method may be used for distinguishing between borneol and isoborneol. The alcohol to be tested is dissolved in about ten times its weight of pyridine, and the calculated quantity of *para*-nitrobenzoyl chloride added, and the mixture heated on a water bath for several hours. The pyridine is removed by extracting with ice-cold dilute sulphuric acid, and the *para*-nitrobenzoate of the alcohol is separated, dried, and recrystallised from alcohol. The borneol compound melts at  $137^{\circ}$ , whilst the isoborneol compound melts at  $129^{\circ}$ .

**BORNYL ACETATE.**—Borneol itself occurs in the free state to a large extent in certain pine needle oils, spike lavender oil, etc. Its acetic ester, bornyl acetate,  $C_{10}H_{17}O_2C.CH_3$ , is found in certain pine needle and other oils, and is a substance of very refreshing odour, recalling that of a pine forest. It is manufactured artificially by the esterification of borneol by acetic anhydride, and, when pure, is a crystalline solid melting at  $29^{\circ}$ , of specific gravity about 0.990. Its refractive index is 1.4645 at  $15^{\circ}$ , and boiling point  $98^{\circ}$  at 10 mm. pressure. When liquefied, it often remains liquid without solidifying for a considerable period. The commercial article is a mixture of bornyl and isobornyl acetates, having an optical rotation about  $+20^{\circ}$ .

**BORNYL BUTYRATE.**—This ester, of the formula  $C_{10}H_{17}O_2C.C_3H_7$ , is very similar to the acetic ester, but is rather more camphoraceous in odour. It is a liquid boiling at  $121^{\circ}$  at 10 mm., and having a specific gravity 0.996; optical rotation,  $+22^{\circ}$ ; and refractive index, 1.4638 at  $15^{\circ}$ .

**BORNYL FORMATE.**—This ester,  $C_{10}H_{17}OOCH$ , is manufactured artificially, and is a liquid of specific gravity 1.013; refractive index, 1.4708; and boiling point,  $90^{\circ}$  at 10 mm. pressure. It has a refreshing pine odour, and is useful for blending with borneol and all its esters. The commercial article is a mixture of bornyl and isobornyl formates, having an optical rotation about  $-47^{\circ}$ .

**BORNYL PROPIONATE.**—Although obtainable commercially, this ester,  $C_{10}H_{17}O_2C.C_2H_5$ , is not often used in perfumery, as it does not differ very materially in odour from the butyrate. It is a liquid of specific gravity 0.978; optical rotation,  $+24^{\circ}$ ; and refractive index, 1.4643. It boils at  $110^{\circ}$  at 10 mm.

**BORNYL VALERIANATE.**—No higher ester of borneol is manufactured than this body, which actually is principally the

isovalerianate of the formula  $C_{10}H_{17}O_2C.C_4H_9$ . It is a liquid having a specific gravity about 0.956; optical rotation,  $+15^\circ$  to  $+20^\circ$ ; refractive index, 1.4628; and boiling point,  $130^\circ$  at 10 mm. It has a rather more fruity odour than the lower esters of borneol.

**BORONIA, OILS OF.**—*Boronia thujona* is a tall shrub growing in New South Wales. The leaves and terminal branchlets yield about 0.5 per cent. of an essential oil which is colourless, with a slight fluorescence, and an exquisite odour of black currants. It has a specific gravity 0.912 to 0.915; optical rotation,  $+13^\circ$  to  $-56^\circ$ ; and refractive index, 1.4524 to 1.4569. It contains 80 to 90 per cent. of thujone, thujol, esters, a sesquiterpene, and a paraffin hydrocarbon. H. G. Smith (*Proc. Roy. Soc. Victoria*, 1919, 32, i.) has examined the oil from *Boronia pinnata*, which has a rose-geranium odour. It has the following characters:—

Specific gravity at $15^\circ$	1.0197
Optical rotation	$+3^\circ 8'$
Refractive index at $20^\circ$	1.5125
Saponification number (on heating)	20.2
Saponification number (in the cold)	18.3
Geranyl acetate	6.4 per cent.
Saponification number on heating, after acetylation	36.9
Saponification number after acetylation in the cold	27.7

According to the author, the oil of *Boronia pinnata* contains free and combined geraniol as acetate and butyrate, trimethyl-gallic acid, and 70 per cent. of elemicine.

**BOSWELLIA RESIN.**—This important gum resin, known as olibanum or frankincense, is of considerable value to the perfumer, and is used, as its common name would imply, in the manufacture of incense. The name olibanum is to some extent of common origin with that of gum benjamin (*q.v.*). It is derived from the Hebrew word *lebonah*, meaning milk, through the Arab *Luban*, meaning incense, and was known to the Greeks as *Libanos*, and to the Romans as *Olibanum*. E. M. Holmes (*P. & E. O. R.*, 1916, 79), in a paper dealing exhaustively with this substance, quotes the following method of trading between the natives who collect gold and the traders, who do not understand each other's languages. "The gold caravan, which consists of some 500 traders, arrives in the highlands of Abyssinia, and brings with it salt

and iron and cattle, and set up a hedge against which they place joints of meat, salt and iron, and then retire. The natives then approach, and each places what gold he considers adequate on what he fancies. They, too, then retire. The traders then return and inspect what has been offered. If content, they remove the gold and leave the goods in exchange; otherwise, they again retire and leave the natives to again approach. This they do, and either place more gold on the goods or take what they had previously left, if they do not consider the goods of any higher value." The collection of frankincense in the early days appears to have been carried out on a similar basis. According to Holmes (*loc. cit.*), the libanotophoros or frankincense-yielding region of the old Sabæans in Arabia was visited by Carter in 1844-1846, and is stated by him to extend on the southern coast from 52° 47' to 58° 28' E. longitude, and a frankincense tree found there was described and illustrated by him in the *Journal of the Bombay Branch of the Royal Asiatic Society*, vol. 11, tab. 23, and subsequently named after him as *Boswellia Carteri* by Dr. (now Sir G.) Birdwood.

Whether the ancient Sabæans derived any portion of frankincense from the opposite coast of Africa, now known as Somaliland, is uncertain, although they were in the time of Solomon (1000 B.C.) in constant communication with the natives of that region, but that it did produce olibanum was undoubtedly known to the Romans in the time of Strabo and Arrian of Alexandra, since the latter (A.D. 54-68) states in the "Periplus of the Erythræan Sea" that olibanum was exported thence, partly to Egypt and partly to Barbaricon, at the mouth of the Indus. At that period the whole of the coast of modern Somaliland from Zeyla (then called *Aulites*) to Cape Gardafui (then called *Promontarius Aromatum*) was known as Barbarica, and the eastern portion of it as *Regio Cinnamomifera*, where cinnamon was supposed to be produced, since the Romans imported it from the port of Mosyllum on that coast. This should not be surprising, since in modern times myrrh was called "Turkey myrrh," and rhubarb "Turkey and East Indian rhubarb," long after their geographical source was known, and, similarly, Goa powder is now known not to be produced at Goa in India, but in Brazil. It seems probable, though it is not certain, that during the Roman occupation of Egypt the trade in frankincense, which was previously centred in Moscha, near Dhofar, the ancient emporium on the south Arabian coast, may have been diverted to Mosyllum,

a port on the opposite African coast, which was in the very centre of the African frankincense-bearing region.

The authors of "Pharmacographia" (1879) state that, at that date, the olibanum of Arabia was shipped from several small places on the Arabian coast between Damkote and Al Kammar, but "the quantity produced in this district is much below that furnished by the Somali country in Eastern Africa." The Somali frankincense is shipped from Bunder Murrayah, Berbera, and many smaller ports to Aden, or direct to Bombay. The trade is chiefly in the hands of the Banians, and the great emporium of the drug is Bombay, but a certain portion is shipped through the Straits of Bab-el-Mandeb to Jiddah, according to Von Kremer, to the value of £12,000 annually.

It does not seem clear from the context whether the native Arabs still collect frankincense in southern Arabia, since the authors quote the statement of Captain Miles (*Jour. Roy. Geog. Soc.*, 1872, vol. xxii., p. 65) that the drug is not collected by the people of the country, but by Somalis, who cross over in numbers to the Arabian coast, paying the Arab tribes for the privilege, and, further, that it would even appear that the names of *Luban Maheri*, or *Mascati*, or *Sheehaz*, referring to places on the coast of Arabia between 52° 10' and 54° 32' E. longitude, are now applied to olibanum brought from the opposite African coast. The authors also state that "Hildebrandt informed one of us (December, 1878) that he has ascertained at Aden that all the frankincense imported into Aden comes from Africa."

The latter statement does not quite agree with that of Vaughan, who in 1853, in a paper on "The Drugs observed at Aden" (communicated by D. Hanbury to the *Pharm. Jour.* (1), xii., p. 229), states that a large quantity of olibanum is collected in the southern and south-eastern districts of Arabia and exported from several towns on the coast between Ras Fartak and Marbat, the famous thuriferous region which proved the object of such diligent search in ancient times.

Vaughan also describes several commercial sorts of African frankincense occurring in the Aden bazaar, and there known by the names of *Luban Mattee*, *Luban Makur*, and *Luban Berbera* or *Mustika*, named after the ports from which they are exported to Aden. The most important of these are: (1) *Luban Berbera*, which is collected by the Ayil Yunis and Ayil Hamed tribes in the west of Somaliland and brought in to Berbera; (2) *Luban Hunkur* or *Aungure*, collected by the Dour Mohammed and

Abardagahala tribes in central Somaliland and brought to the port of Aungure ; (3) the *Luban Makur*, which is collected in the east of Somaliland by the Worsungali and Meggertein Somalis in May, June and July, and carried to the neighbouring ports, such as Bunder Koor and Bunder Kassoom, and is nearly all taken across to Maculla and Shehr, on the Arabian coast. This possibly comes back to Aden as the *Luban Shaharree* or *Luban Morbat*, supposed by Vaughan to be produced in Arabia.

The *Luban Mattee* described by Vaughan is collected chiefly by the Abardagahala tribe in central Somaliland and brought to the port of Maiti, near to the ancient Mosyllum, for export, whence the name of *Luban Matti* or *Mayeti*.

Vaughan also distinctly affirms that three *baggalas* were annually freighted from Marbat to Bombay with an entire cargo of the Arabian frankincense, which realises a higher price in the market than any of the qualities exported from Africa. The only probable explanation of these contradictory statements is that frankincense is collected in Arabia by Somalis and exported direct to Bombay, and that some of it is sent back from Bombay to Aden *en route* for Europe.

The latest account of the frankincense region of Somaliland is given by Dr. E. Drake-Brockman, F.R.G.S., in "British Somaliland" (1914). He states that the drug is produced in the coast regions, more especially those occupied by the Habr Toljaala, Warsangali, and Mijertain tribes, and that the drug is known to the Somalis as *Beyo* or *Hanjibeyo* ; also that there are two distinct varieties, called by the Arabians *Loban Dakar* and *Loban Maidi*, i.e., male and female frankincense respectively. The tree yielding *Loban Dakar* is called by the Somalis *Mohor* or *Mohur*, and is *Boswellia Carteri*, whilst the tree yielding *Loban Maida* is called *Yehar*, and is *Boswellia Frereana*.

The former is found on the maritime limestone mountains eight miles south of Berbera in western Somaliland, and thence eastwards, whilst *Boswellia Frereana* is not found until the Habr Toljaala country is reached, and extends further west into the country of the Warsangali and Mijertain tribes.

*B. Carteri* was first described by Speke as a tree with rugged bark and smooth epidermis of a reddish tinge, pleasant aromatic odour, and strong astringent flavour, and as used for tanning skins. Powdered and sprinkled dry on a wound, it acted as a styptic. Dr. Drake-Brockman describes the freshly collected drug as follows : Both the varieties are found in small tears, and



are mixed up with bark, sand, and other foreign matters, and have to be sorted, which is usually done at Aden, the picked samples of *Loban Dakar* being sent to Europe, whilst the *Loban Maidi* is sent to India and Egypt. The inferior qualities of each are done up separately in sacks of matting and shipped back to Africa most of it finding its way to Abyssinia. The *Loban Dakar* is shipped from Aden to London and Hamburg, where it is made into false amber beads, which are threaded into necklaces and rosaries, much worn by the Arab and Somali women. The tears of the two kinds are not difficult to distinguish, the tears of *Loban Dakar* being usually darker and of a more amber colour; the tears of *Loban Maidi* are paler and clear like a topaz. The latter, when packed, generally becomes formed into large masses, whilst the *Loban Dakar*, being drier and more friable, does not usually conglomerate so readily, and does not form so plastic a mass when chewed. In the form of emulsion, it is sometimes given for venereal complaints. The *Loban Maidi* is chewed by the Somalis, and is sometimes used in the chewed state as a cement. A variety of *Loban Maidi* is sometimes found in large stalactitic pieces formed by the oozing and trickling down of the milky juice. These pieces may be 6 inches or more long and 3 or 4 broad, and present a characteristic appearance, having an irregular surface with many small protuberances and being covered with white powdery streaks, and, when fractured, showing alternate white and clear layers, and on the under surface often have pieces of the papery outer bark attached.

The colour varies in both kinds, being often pale in the *Loban Dakar* and deep orange in the *Loban Maidi*. The *Loban Dakar* is sometimes found in pieces the size of a hen's egg, but is then invariably composed of small agglomerated tears.

As regards the name *Beyo* and *Hanji-beyo*, Dr. Drake-Brockman explains that the prefix *Hanji* is applied to any gum resin that is used for chewing. It therefore applies more strictly to the *Loban Maidi*, which is used for that purpose.

In Bombay frankincense passes through the Custom House under the name of *Esesh* (*Isas* of Drake-Brockman), and is there sorted into four or five different qualities, the first, consisting of large clear tears, being destined for the European market. The intermediate qualities, as well as the last, known by the Indian name of *Dhup*, consisting of pieces of the bark coated with frankincense, supply the Indian or Chinese market.

The Mahometan writers describe five kinds under the Sanscrit

name of *Kundur*, as follows : (1) *Kundur Zakar*, or male frankincense, in deep yellow tears ; (2) *Kundur Unsa*, or female frankincense ; (3) *Kundur Madahraj*, artificial tears made by shaking the moist exudation in a basket ; (4) *Kundur Kishar*, or *Kashfar*, consisting of pieces of bark covered with the exudation, identical with the *Dhup* already mentioned ; (5) *Kundur Dukak*, or dust of olibanum. In the London market there are three principal forms recognised : ordinary, consisting of irregular or more or less oval or pyriform tears, and garblings and siftings. The fine large tears known at Aden as *Luban Fasons Bedow* come from the Mijertain district, in the east of Somaliland. The *Luban Maidi* of Drake-Brockman comes from the same district, but is not a regular article of importation into this country. A very fine specimen of it exists in the museum of the Pharmaceutical Society at Bloomsbury Square, presented some years ago by Mons. César Chantre, a French silk merchant, then residing in London, a native of Lyons, who made a hobby of the study of the London drug market, and acquired a fine collection, which he subsequently presented to Dr. Cauvet, a professor of materia medica in his native city, who published a few years afterwards a little known, but most concise, reliable, and almost encyclopædic work on materia medica.

Until the middle of the last century but little was known to botanists concerning the trees that yield the olibanum of commerce. In 1846 Dr. J. Forbes Royle suggested, in an article in the *Pharmaceutical Journal*, vol. v., p. 543, that African olibanum was probably the produce of a species of *Boswellia* of the natural order *Burseraceæ*. It was only in 1870 that Dr. (now Sir G.) Birdwood was able to describe as sources of olibanum, *Boswellia Carteri*, obtained by H. J. Carter in 1848 on the south-east coast of Arabia ; *Boswellia Bhan-Dajiana*, obtained by Colonel Playfair ; and *Boswellia Frereana*, from eastern Somaliland, the last-named being the source of the rarer frankincense known by the Arab name of *Luban Maidi*, *Mattee*, or *Mayeti*. The species are not the only ones that yield frankincense, since there are several others mentioned in "Pharmacographia" from which it is collected, but it is doubtful whether they are species or only forms growing under different conditions, some of them occurring on limestone hills and valleys in the neighbourhood of the sea, sometimes in limestone detritus, and others growing out of the rocks on the high and precipitous mountain ranges further inland.

One of those referred to, *B. Carteri*, is called by the natives *Mohr*

*Meddu* or *Madow*, i.e., black mohr tree, and another referred to, *B. Frereana*, is called *Makar* in Sennaar. Dr. Malcolmson describes one of these as growing at about 1,000 feet on the hills near Bunder Marrayah ( $11^{\circ} 43' N.$  latitude) to a height of 40 feet, firmly attached to the bare limestone by a mass of vegetable substance, part of the tree, which sends roots into the crevices of the rock to an immense depth.

The trees have pinnate leaves recalling in appearance those of the mountain ash, but hairy, the branches having panicles of small fragrant greenish flowers. The whole plant contains the fragrant gum resin, which exudes even from the flowers, when injured, as a milky juice. The collection of the frankincense is described by Cruttenden, who visited the Somali country near Bunder Munrayah in 1843, as follows: "About the end of February or the beginning of March, during the hot season, the Bedouins visit all the trees in succession and make a deep incision in each, peeling off a narrow strip of bark for about 5 inches below the wound. This is left for a month, when a fresh incision is made in the same place, but deeper. A third month elapses, and the operation is again repeated, after which the gum is supposed to have attained a proper degree of consistency. The mountain sides are immediately covered with parties of men and boys, who scrape off the large clear globules into a basket, whilst the inferior quality that has run down the tree is packed separately. The gum, when first taken from the tree, is soft, but hardens rapidly. Every fortnight the mountains are visited in this manner, the trees producing larger quantities as the season advances, until the middle of September, when the first shower of rain puts a close to the gathering for that year."

The collection of the drug in southern Arabia is described by Carter as follows: "The gum is procured by making longitudinal incisions through the bark in the months of May and December, when the cuticle glistens with intumescence from the distended state of the part beneath. On its first appearance the gum comes forth white as milk, and, according to the degree of fluidity, finds its way to the ground, or concretes on the branch near the place from which it first issued, whence it is collected by the men and boys employed to look after the trees by the different families who possess the land in which they grow."

Hildebrandt, speaking of the collection of *Luban Meithi*, *Maiti*, or *Maidi*, near Lasgori, in Somaliland, from the *Gekar* (*Yegaar*) trees, states that the thick, low trunk of the tree grows out of the

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nearly perpendicular rock, and that the flowers were just blossoming on March 25th. The Somali men and women reach the trees by very dangerous paths, and make incisions, and after only six days collect the resin. The *Luban Maiti* does not contain gum, but only oil and resin, and therefore probably dries more quickly than the ordinary frankincense. He remarks that it is sold at Aden and Geddah (Djedda), and thence finds its way as a masticatory to the harems, and is also chewed by the Somalis when they are tired.

It is noteworthy that it does not seem to have been utilised for this purpose, for which its pleasant odour and possibly antiseptic properties should render it useful.

Pure olibanum has, according to Kremel, the following characters :—

	1	2	3
Percentage of resin . . .	64	72.1	67
Acid value of resin . . .	59.3	46.8	50.3
Ester value of resin . . .	6.6	41.0	60.5
Saponification value of resin . .	65.9	87.8	110.8

Sample No. 1, however, is probably quite abnormal.

Olibanum contains a small amount of essential oil, varying from 5 to 10 per cent., which is a pale yellow liquid of balsamic odour, having a specific gravity 0.875 to 0.894; optical rotation,  $+15^{\circ}$  to  $+30^{\circ}$ ; and refractive index, 1.4725 to 1.4825. It contains  $\alpha$ -pinene, camphene, dipentene, *para*-cymene, and an alcohol of the formula  $C_{10}H_{16}O$  which has been named olibanol. Borneol esters are present in traces.

*Boswellia serrata* is a native of north-west India, and yields a somewhat similar resin. Apparently there are two well-recognised varieties, the *foliola ovato-oblonga* and the *foliola lineari-lanceolata*. The resin is collected in the Punjab twice a year. It is used for medicinal purposes, and is also burned as incense in religious ceremonies. Experiments have been carried out recently at the Forest Research Institute at Dehra Dun with a view to determining the most advantageous method of treating the crude gum resin in order to separate the essential oil, the purified resin, and the gum. The crude gum resin is placed in a still with a perforated false bottom, and steam is passed through the mass. Most of the resin and oil passes through, and collects at the bottom

of the still, whilst the gum and impurities remain on the false bottom. The oil is then separated from the resin by steam distillation, and the oil so obtained is rectified, and then consists of almost pure pinene. From experiments on this oil carried out at the Imperial Institute it was found that this oil dissolves varnish resins, such as dammar, sandarac and soft copal, and varnishes prepared with it dried with a less lustrous surface, but more rapidly, than those made with ordinary turpentine.

Tinctures of olibanum are used as fixatives, and also in the preparation of heavy Oriental odours. Perfumes containing champaca and perfumes of the broom type are improved by traces of olibanum. Olibanum is sometimes known as gum Thus. (See also under "Incense.")

**BOUVARDIA.**—This is a fancy name, of considerable popularity, for a perfume somewhat resembling jasmin in type. It is based on such synthetic perfumes as benzyl acetate, hydroxycitronellal and phenyl-ethyl acetate.

**BRILLIANTINES.**—These are merely mixtures of perfume and oil used as dressings for the hair. They are usually mixtures of an alcoholic solution of perfume with olive, almond, castor or petroleum oils, which require shaking before use, or are simply these or similar oils to which a trace of absolute perfumes, free from alcohol, has been added, thus forming a one-solution brilliantine.

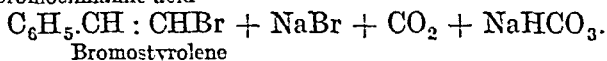
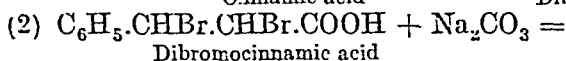
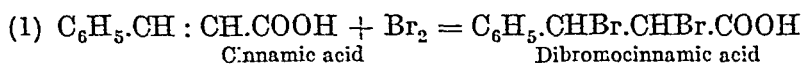
**BRISBANE WHITE SASSAFRAS, OIL OF.**—The tree known in Queensland as the white sassafras is a species of cinnamon, *Cinnamomum oliveri*. The bark yields an essential oil of specific gravity 1.030, and refractive index 1.5165 at 23°. It contains about 12 to 15 per cent. of pinene, 18 to 20 per cent. of camphor, 25 to 27 per cent. of safrol, and 40 to 45 per cent. of eugenol methyl-ether (*Jour. Chem. Soc.*, 1916, 751).

**BROMACETAL.**—Bromacetal is an important intermediate product in the manufacture of phenyl-acetic aldehyde, the well-known artificial hyacinth base. It has the formula  $\text{CH}_2\text{Br}.\text{CH}(\text{O}.\text{C}_2\text{H}_5)_2$ , and boils at 82° at a pressure of 28 mm. It results by adding, very gradually, 51 c.c. of bromine to 45 grams of paraldehyde kept at a temperature of some degrees below freezing point. After the crystalline mass has liquefied, 200 c.c. of absolute alcohol are added and the mixture allowed to stand for twelve hours. Bromacetal is not itself used as such in perfumery.

**BROMELIA.**— $\beta$ -naphthol-methyl-ether and  $\beta$ -naphthol-ethyl ether are two well-known artificial perfume materials which are known as nerolin. The former is also known as yara-yara, whilst the ethyl ether is known as bromelia. These bodies have the formula  $C_{10}H_7O.R$ , where R is the methyl or ethyl radicle.

Both have a pronounced neroli odour, that of the ethyl ether being rather the finer, with a suggestion of pineapple. Yara-yara melts at  $72^\circ$ , and bromelia at  $37^\circ$ . They may be prepared by heating  $\beta$ -naphthol-sodium with methyl (ethyl) iodide in methyl (ethyl) alcohol. One thousand parts of 90 per cent. alcohol dissolves about 20 grams of yara-yara, and 40 grams of bromelia.

**BROMOSTYROLENE.**—This body, of the formula  $C_6H_5.CH:CHBr$ , is a very important synthetic perfume. It is used to a very considerable extent (as is also phenyl-acetic aldehyde (*q.v.*)) as the basis of perfumes of the type of hyacinth, narcissus and jonquil. It is employed very extensively in soap perfumery. Styrolene,  $C_8H_8$ , yields two series of halogen derivatives, the  $\omega$ -derivatives and the  $\alpha$ -derivatives. For example,  $\omega$ -bromostyrolene is  $C_6H_5.CH:CHBr$ , and  $\alpha$ -styrolene is  $C_6H_5.CBr:CH_2$ . The  $\alpha$ -derivatives are useless for perfumery purposes, while the  $\omega$ -compounds are highly odorous.  $\omega$ -Bromostyrolene is prepared by treating cinnamic acid with bromine to saturate the double linkage, and a molecule of hydrobromic acid is abstracted by means of caustic alkali. Lewinsohn (*P. & E. O. R.*, 1924, 119) gives the following method for its manufacture. Bromostyrolene is formed from cinnamic acid according to the following equations:—



Ten kilograms of cinnamic acid and 40 kg. of ether are placed in a mixing vessel, which is provided with an exceptionally good condenser, having a large cooling surface. A means of injecting live steam is also provided.

Eleven kilograms of bromine (3,670 c.c.) are then slowly introduced by means of a dropping funnel during continuous stirring and strong cooling of the reflux condenser. When the addition of the bromine is complete, the stirring is continued for some hours, and the ether distilled off—the condenser being

connected to the still by means of a three-way cock, so as to allow this operation to be conducted by merely turning the cock. As soon as the ether has been completely removed, a solution of 7 kg. of soda ash in 20 kg. of water is added, and the reaction mixture steam distilled. The bromostyrol distils over with the water and collects on the bottom of the receiver. It is rectified under diminished pressure. Boiling point, 98° to 99° at 5 mm. Bromostyrol turns brown in daylight, and must be kept in the dark.

$\alpha$ -Bromostyrolene,  $C_6H_5CBr : CH_2$ , is a very unstable substance, of no value in perfumery. The commercial article,  $\omega$ -bromostyrolene,  $C_6H_5CH : CHBr$ , can, theoretically, exist in two stereoisomeric forms.

Dufraisse (*Comptes Rendus*, 1920, 171, 960) has prepared the second isomer by the action of caustic soda on bromobenzalacetophenone. According to Dufraisse the two stereoisomers have the following characters:—

	Commercial $\omega$ -bromostyrolene.	Stereoisomeric variety.
Specific gravity at 20°	1.4220	1.4260
Refractive index	1.6094	1.5990
Boiling point at 22 mm.	107°	71° (at 6 mm.)
Boiling point at 760 mm.	220°	—
Melting point	+ 7°	— 8°

A. G.

**BROOM.**—The flowers of *Sarothamnus scoparius*, and possibly allied plants, are cultivated in Provence, and the perfume extracted, in the form of concrete or absolute, by means of volatile solvents. The perfume, known as “genêt,” is also known as an artificial preparation, which usually contains some natural perfume and various synthetics, including *para*-cresol methyl ether.

**BRUYÈRE D'ANNAM.**—*Bacckea frutescens* is a plant found in southern China and in Cochin China, where it is known as *Bruyère d'Annam*. It yields an essential oil having a specific gravity 0.890; optical rotation,  $-4^{\circ} 34'$ ; refractive index, 1.4754; acid value, 1.9; ester value, 3.7; and ester value after acetylation, 44.8. It probably contains linalol and cymene. Eucalyptol is also present. This oil has also been described as “essence de Bruyère de Tonkin.” The plant is in full flower in August. Distillation commences in January, and the oil varies to a slight extent with the locality in which it is distilled. It is used in France for the perfuming of soap.

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There appear to be two oils distilled from the plant under different conditions, one oil being yellow and the other green in colour. They have both been examined by Gattefossé, and also by Roure-Bertrand Fils (*La Parfumerie Moderne*, 1923, 108, and *Bulletin*, Roure-Bertrand Fils, April, 1914, 6). The oils had the following characters :—

### Yellow Oil

	Gattefossé.	Bertrand.
Specific gravity at 15° . . . . .	0.8885 ..	0.8862
Optical rotation . . . . .	— 6° 5' ..	— 1° 22'
Refractive index . . . . .	1.4790 ..	—
Esters . . . . .	2.16 per cent.	3.5 per cent.
Free alcohols . . . . .	12.97 „	—
Aldehydes . . . . .	5.2 „	3.5 „

### Green Oil

Specific gravity at 15° . . . . .	0.8895 ..	0.8871
Optical rotation . . . . .	— 0° 6' ..	— 4° 40'
Refractive index . . . . .	1.4772 ..	—
Esters . . . . .	3.6 per cent.	1.2 per cent.
Free alcohols . . . . .	11.3 „	—

Up to 1923 this oil was regarded as the product of *Cathetus fasciculata*, which is now known to be erroneous.

**BUCHU OIL.**—This oil is not used to any extent in perfumery, but in the preparation of flavours having a black currant odour or taste a small amount of it is sometimes employed. There are several species of buchu used for the distillation of the oil, of which the principal are *Barosma serratifolia*, *B. betulina* and *B. crenulata*. The leaves yield from 1 to 2 per cent. of oil. It contains limonene, dipentene, a ketone which is probably *lævo*-menthone, and a crystalline body known as diosphenol,  $C_{10}H_{16}O_2$ , melting at 83°. This body occurs principally in the oil from *B. betulina*. There is a species of barosma, *B. pulchella*, which yields an oil having the odour of citronella. The four oils referred to have the following characters :—

	Specific gravity.	Rotation.	Refractive index.
<i>B. betulina</i> . . . . .	0.935 — 0.970	— 15° to — 48°	1.4740 — 1.4865
<i>B. crenulata</i> . . . . .	0.935	— 15°	1.4800
<i>B. serratifolia</i> . . . . .	0.918 — 0.960	— 12° to — 36°	—
<i>B. pulchella</i> . . . . .	0.885	+ 8° 30'	1.4575



**BULNESIA SARMIENTI.**—This tree yields the wood known as *Palo santo* (holy wood) or *Palo balsama* to the inhabitants of Argentina and Paraguay. The tree grows very freely along the course of the Rio Bermejo, a tributary of the Rio Paraguay. The wood yields from 4 to 8 per cent. of a semi-solid essential oil, which is known as guaiac wood oil or guaiacum wood oil, as it was at one time erroneously believed to be derived from *Guaiacum officinale*. It has also been known in commerce as champaca wood oil. It has a very fine and delicate odour, and is well adapted for blending with more powerful perfumes. Apart from its legitimate use, it is sometimes used as an adulterant of otto of roses. It melts at from 42° to 50°, and has a specific gravity 0.965 to 0.975 at 30°; optical rotation,  $-3^{\circ}$  to  $-8^{\circ}$ ; and refractive index, 1.5030 to 1.5050 at melting point. The only well-ascertained constituent present is the alcohol guaicol,  $C_{15}H_{26}O$ .

**BUPLEUROL.**—This body is an alcohol of the formula  $C_{10}H_{20}O$ . It is found in the essential oil of *Bupleurum fruticosum*. It has a faint rose odour, and has a specific gravity 0.849; optical rotation,  $0^{\circ}$ ; refractive index, 1.4508; and boiling point, 209° to 210°.

**BUPLEURUM FRUITICOSUM.**—This umbelliferous plant grows wild in Sardinia. The flowers and leaves contain an essential oil of specific gravity 0.830 to 0.869; optical rotation  $+19^{\circ}$  to  $+47^{\circ}$ ; and refractive index, 1.4783 to 1.4862. It contains an alcohol, which has been named bupleurol (*q.v.*), which has a slight but distinct odour of roses. (See *Att. R. Accad. Lincei*, 1913, 22, 34.)

**BURSERA OILS.**—See "Linaloe Oil."

**BUTNERIA OCCIDENTALIS, OIL OF.**—The leaves and twigs of this plant, also known as *Calycanthus Occidentalis*, yield a small quantity of a fragrant essential oil of specific gravity 0.930; optical rotation,  $+7^{\circ}$ ; and refractive index, 1.4710. It contains eucalyptol, pinene, borneol, linalyl acetate, camphor, methyl salicylate, and a sesquiterpene alcohol.

**BUTYL ESTERS.** (See also "Butyl Phenyl Acetate.")—The esters of butyl alcohol are of a fruity or floral odour, the principal of them having the characters shown in the table on p. 114, as met with in commerce (Durrans, *P. & E. O. R.*, 1924, 226).

**BUTYL PHENYL ACETATE.**—This ester, of the formula  $C_4H_9CO_2.CH_2.C_6H_5$ , is a colourless oil having an odour recalling that of carnation. It is only used in small quantities, and gives

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	Specific gravity.	Refractive index.	Boiling point.
Butyl acetate . .	0.880-0.882	—	123°-127°
„ benzoate . .	1.0085-1.0090	1.4975-1.4980	247°
„ butyrate . .	0.871	1.4050	160°-165°
„ formate . .	0.9108	—	106°-107°
„ phenyl acetate .	0.9969	1.4890	260°
„ propionate . .	0.8828	—	145°-146°
„ salicylate . .	1.076	1.5110	266°-267°
„ valerianate . .	0.8648	1.4109	170°-175°

character to the various types of carnation bouquets. Its isomer, isobutyl phenyl acetate, is of a much finer odour, and is known as “eglantine” or “ideal base.” It is used as the basis of most perfumes offered under the name “eglantine,” and is also useful in carnation and rose odours. It has a specific gravity 1.104, and refractive index 1.5570.

**BUTYRIC ALDEHYDE.**—Butyric aldehyde,  $C_3H_7.COH$ , is an aldehyde with a pronounced sharp odour, occurring in oils of eucalyptus and cajuput. It is a liquid, boiling at 75°.

**BUTYRIC ETHER.**—See “Ethyl Butyrate.”

**CABRIUVA WOOD OIL.**—*Myrocarpus fastigiatus* is a member of the natural order *Leguminosæ*, a native of Brazil. It is known locally as *cabriuva*. The flowers are yellowish-white and of great fragrance. Their odour resembles that of a mixture of vanilla and frankincense or tolu balsam. The wood is highly valued in Brazil.

*Schimmel & Co.* (Report, April, 1896, 64) examined the oil, and found it to have a specific gravity 0.9283, and optical rotation  $-8^{\circ} 29'$ .

**CABUREIBA BALSAM OIL.**—*Myrocarpus frondosus* and *M. fastigiatus* (see also “Cabriuva Wood Oil”), both natives of Brazil, and belonging to the natural order *Leguminosæ*, yield a balsam from natural as well as from artificially produced wounds. The balsam is reddish-brown, and greatly resembles Peru and tolu balsams, both in appearance, consistency and odour. It contains benzoic acid, both free and combined in the form of esters. Vanillin is also present in traces.

**CADE, OIL OF.**—See “Cadinene.”

**CADINENE.**—This sesquiterpene is found principally in oil of cade, the product of the destructive distillation of the wood of *Juniperus oxycedrus*. From the tar so produced, a refined oil can be obtained by steam distillation. This is a dark yellow viscid liquid of specific gravity 0.915 to 0.930, and optical rotation about  $-30^{\circ}$ . It contains much cadinene,  $C_{15}H_{24}$ , a liquid of specific gravity 0.921; optical rotation,  $-105^{\circ}$ ; refractive index, 1.5065; and boiling point,  $273^{\circ}$  to  $275^{\circ}$ . Cadinene yields a fine blue colour when a few drops are dissolved in chloroform and the liquid shaken with a few drops of concentrated sulphuric acid. It is present in numerous essential oils, including patchouli, cedar wood, West Indian sandalwood, and others. It is used in small amount in perfumery, and has been recommended as a constituent of artificial ylang-ylang oils.

**CALAMINE.**—Calamine is essentially zinc carbonate, and is used in the preparation of dusting powders and face lotions. Originally the term calamine indicated the natural mineral very finely powdered. It is a heavy powder of a brownish to pink colour, consisting of zinc carbonate, with varying quantities of zinc silicate and traces of iron oxide as impurities. To-day the calamine of commerce is usually artificially precipitated zinc carbonate, with varying proportions of zinc oxide and traces of ferric oxide to colour it. The only important feature for the perfumer is that it should be finely powdered, free from gritty particles, and should consist almost entirely of zinc carbonate,  $ZnCO_3$ , and be soluble in hydrochloric acid with the exception of a small amount—not more than 3 to 5 per cent. in the best samples.

**CALAMINTHA OILS.**—*Calamintha nepeta* (*Satureja Calamintha*) is a plant flourishing in Calabria and Sicily, and from which the essential oil has been distilled. The plant is known as "false mint," or "nepitella." Sicilian plants examined by Roure-Bertrand Fils (*Bulletin*, October, 1912, 68) yielded 0.14 per cent. of essential oil. Umney and Bennett also examined a Sicilian oil (*Chemist and Druggist*, 67, 970). The figures obtained for these two samples were as follows:—

	Roure-Bertrand.	Umney.
Specific gravity	0.925	0.922
Optical rotation	$+17^{\circ} 48'$	$+14^{\circ}$
Esters.	4.4 per cent.	4.2 per cent.
Alcohols (as menthol)	14	18.2
Ketones	20	10.8

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La Face has recently examined authentic samples of this oil, and found quite similar figures, although a sample of French grown oil is reported as having a specific gravity 0.982; optical rotation,  $+ 3^{\circ} 5'$ ; and refractive index, 1.5115 (*La Parfumerie Moderne*, 1923, 162).

*Calamintha umbrosa* grows wild in certain localities in Travancore, and is known locally as *karimthumba*. K. L. Moudgill (*Jour. Soc. Chem. Ind.*, May 23rd, 1924) distilled a quantity of fresh leaves with steam, when a 0.35 per cent. yield, calculated on the dry leaves, of a light yellow oil possessing a strong rather complex, but not unpleasant odour, was obtained. The oil had the following characters:  $d_{4}^{27}$ , 0.8854;  $n_D^{27} = 1.4760$ ;  $[\alpha]^{239} = -45.2^{\circ}$ ; acid value, 0.5; ester value, 15.9; ester value after acetylation, 40.7; aldehydes by the neutral sulphite method, 6.5 per cent. The oil was insoluble in 80 per cent. alcohol, sparingly soluble in 85 per cent. alcohol, soluble in 90 per cent. alcohol. In view of the low density and refractive index of the oil, the difficulty with which it dissolves, even in 85 per cent. alcohol, and the ester values, it would appear to consist mainly of hydrocarbons. The oil dried over anhydrous sodium sulphate was distilled under reduced pressure, first over a boiling-water bath (fractions 1 to 3), and then rapidly over a free flame, and the following fractions were obtained:—

No.	Boiling point.	Pressure. mm.	Yield per cent.	$n_D^{27}$	$\alpha_D^{30}$
1	To 80° . .	26	20	1.4687	— 62.5°
2	80°–85° . .	26	32	1.4665	— 68.3°
3	Above 85° . .	26	14	1.4695	— 53.8°
4	105°–110° . .	17	27	1.4900	— 5.2°
5	Residue and loss (by diff.) . .	—	7	—	—

Fractions 1, 2 and 3 would appear to contain the same compound. Fractions 1 and 2 were mixed and distilled repeatedly over sodium under atmospheric pressure, and finally 12 c.c. of a colourless oil were obtained, of boiling point 176° to 177°;  $d_{4}^{27}$ , 0.8565;  $n_D^{27} = 1.4700$ ;  $\alpha_D^{30} = -73.35^{\circ}$ . *l*-Limonene has boiling point 175° to 176°;  $d$ , 0.8472;  $n_D^{27} = 1.4746$ ;  $\alpha_D^{30} = -105^{\circ}$ . Bromination of the oil yielded a halogen derivative which proved to be *l*-limonene tetrabromide. In spite of repeated

fractionation and distillation over sodium, the *l*-limonene separated from this oil was heavier, but had a higher refractive index than pure *l*-limonene, probably due to the presence of small quantities of another hydrocarbon, which, however, could not be separated.

*Fraction 4.*—The aldehyde content of this fraction was found by the sodium bisulphite method to be 10 per cent. The residual oil had  $n_D^{28} = 1.4930$ ;  $\alpha_D^{30} = +5.4^\circ$ ;  $d_{40}^{28} = 0.9293$ . It was soluble in 3.4 volumes of 75 per cent. alcohol.

**CALYCANTHUS OIL.**—The air-dried stems of *Calycanthus floridus* yield a small quantity of an odorous essential oil, which has been examined by Miller, Taylor and Eskew (*Jour. Amer. Chem. Soc.*, 36, 2182). Pinene, cineol, bornyl acetate and other esters are present in the oil, and probably linalol and sesquiterpenes. Three samples had the following characters:—

	1	2	3
Yield . . . . .	0.53 per cent.	0.25 per cent.	0.39 per cent.
Specific gravity at 25° . . . . .	0.9209	0.9161	0.9136
Optical rotation . . . . .	+ 2.85°	+ 2.84°	+ 6.6°
Refractive index at 26° . . . . .	1.4675	1.4713	1.4753
Saponification value . . . . .	12.5	14.4	16.6
Saponification value after acetylation . . . . .	75.1	—	65.7
Total alcohols, as borneol . . . . .	18.44 per cent.	—	14.46 per cent.
Esters, as bornyl acetate . . . . .	4.37 „	5.04 per cent.	5.81 „
Cineol . . . . .	35 „	—	70 „

**CAMPHOR AND CAMPHOR OIL.**—Camphor is a constituent of numerous essential oils used in perfumery, but, as such, is only used in the industry for the preparation of such substances as camphor ice, etc. Camphor oil, however is of great importance as the source of supply of a very important raw material of the perfume industry, namely, safrol (*q.v.*). The tree yielding camphor oil is *Cinnamomum camphora*. It is widely distributed throughout the eastern provinces of central China, on the island of Hainan, and very extensively in Formosa. It also occurs as a forest tree on the islands of Kiushiu and Shikoku. The greater part of the camphor produced comes from Formosa, and the industry is practically a Government monopoly. The tree is felled and the young branches and twigs are chopped up and placed in perforated

jars and heated over steam. The steam saturates the fragments, and the crude camphor sublimes into earthenware pots placed over the jars. The crude material is pressed and separated into a slightly more refined camphor, and a certain amount of camphor oil. The greater part of the camphor oil of commerce is, however, obtained by direct distillation of the chips in crude stills. The oil is drained from the separated camphor, but still retains a considerable amount in solution. Redistillation is resorted to until it does not pay to separate the camphor any further. So that, in fact, solid camphor is really only a fraction of the entire "camphor oil," and the camphor oil of commerce is really only the residual fractions after the extraction of most of the camphor.

Camphor,  $C_{10}H_{16}O$ , is the ketone of the alcohol borneol (*q.v.*), and occurs in the essential oil as *dextro*-camphor, the rare *laevo*-camphor being found in the oil of *Matricaria parthenium*. It forms a translucent mass, obtainable in coarse powder by sublimation, of specific gravity 0.985; melting point,  $176^{\circ}$  to  $179^{\circ}$ ; boiling point,  $205^{\circ}$  to  $207^{\circ}$ ; and specific rotation,  $44^{\circ}$ . It is freely soluble in organic solvents (alcohol, 1 in 1; chloroform, 4 in 1; ether, 2 in 1). It occurs in commerce in coarse powder (flowers of camphor), in bell-shaped masses (bell camphor), or in small tablets of varying sizes. In the semi-refined condition it is also imported in the form of large slabs.

The crude camphor oils of commerce exist in, roughly, four different varieties. These are as follows:—

(1) The crude oil as it leaves the distillery, with as much camphor separated as possible. This has a specific gravity 0.950 to 0.998.

(2) Heavy camphor oil, or brown camphor oil, which is the crude oil from which the low-boiling terpene fractions have been as completely removed as possible. This oil is rich in safrol. Specific gravity, 1.000 to 1.040.

(3) The light oil, consisting of the terpene fraction mentioned under (2). Specific gravity, 0.870 to 0.890.

(4) The very high-boiling fractions, extremely rich in safrol, of specific gravity 1.060 to 1.075, and which is sold as "artificial sassafras oil."

Safrol, obtained from camphor oil, is the raw material from which heliotropin is manufactured.

A very large number of patents have been granted for the manufacture of camphor artificially. A clear distinction must

be made between the true artificial camphor, the so-called "synthetic camphor," and pinene hydrochloride,  $C_{10}H_{16}HCl$ , a crystalline compound of pinene which was known as artificial camphor, on account of its physical resemblance to true camphor, before the artificial production of camphor had been achieved. This so-called artificial camphor is prepared by passing a current of dry hydrochloric acid gas through well-cooled pinene. The resulting crystals melt at  $127^{\circ}$ , and have a camphoraceous odour, and may be used as a substitute for camphor to a certain extent. A complete synthesis of camphor has been achieved by Komppa (*Berichte*, 36, 1332), but has no commercial application. Many processes yield camphor on a reasonably payable scale, but, owing to the fact that the Japanese monopoly is able to control prices, artificial camphor is rarely able to compete with the natural substance. In general, such processes for the production of artificial camphor depend on the conversion of pinene, obtained from turpentine oil, into pinene hydrochloride, which, by abstraction of hydrochloric acid, yields camphene. This is converted into isobornyl acetate by treatment with acetic and sulphuric acids, and is saponified by treatment with alkali, and the resulting isoborneol is oxidised to camphor.

(See also "Sho-Gyu and Yu-Ju Oils"; refer B. J. Eaton, *Dept. of Agriculture, Federated Malay States, Bull.* 15, February, 1912, for attempts at cultivation of camphor trees in Malay States; and see photographs of stills by Monopoly Bureau of Formosa, reproduced in Parry, "The Chemistry of Essential Oils," 4th ed., vol. ii., pp. 158, 159. For the high-boiling sesquiterpene compounds of camphor oil, see Ruzicka and Stoll, *Helv. Chim. Act.*, 1924, 7, 260.)

**CANANGA OIL.**—Oil of cananga and oil of ylang-ylang are obtained from the same botanical source, the superiority of the ylang-ylang oil being due to the different conditions under which the trees grow, and to the methods of distillation. The tree from which the flowers are distilled is *Cananga odorata*, one of the *Anonaceæ*, of which a native name is *Alan-guilan*, or *Ihlang-Ihlang*, meaning the "flower of flowers."

The tree is a native of Ava and Tenasserim, and is generally distributed and cultivated throughout southern Asia. It attains a height of about 60 feet. The flowers are very handsome and conspicuous, bell shaped, of a pale yellow or greenish colour, with a beautiful perfume, often compared with a mixture of hyacinth, narcissus, clove, jasmin and lilac.

## PERFUMERY

The following account of the plant is from the *Perfumery and Essential Oil Record*, 1910, 223 :—

“The plant from which it is derived, *Cananga odorata*, was first described by Rumph in 1750 under its Malayan designation of *Bonga cananga*. It is called *Isjampa* by the Javanese. It is stated to have been first introduced into India from Sumatra in 1797, a description of it in the Botanical Gardens of Calcutta being by Roxburgh (‘*Flora Indica*,’ 1832). It is described by Hooker and Thompson (‘*Flora Indica*,’ 1855). It is illustrated in the ‘*Flora Java*’ by Blume (1829). We are courteously informed by Mr. Prain, the director of the Royal Botanical Gardens at Kew, that no flowering plants are available for photography at the present time. Fluckiger (*Pharm. Jour.*, May 14th, 1881) stated that the incorrect name *Unona odoratissima*—so described from its overpowering odour—originated with Blanco (‘*Flora de Filipinas*,’ Manila, 1845), and for years the oil was described in price lists as oleum unonæ.

“The oil appears to have been sent to Europe first in 1864, when it was offered in Paris. The first shipments were not made from Manila, but the recognition of its beautiful odour resulted in its distillation in Manila, at first by German pharmacists.

“*Cananga odorata* attains a height of 60 feet, has few, but much ramified, branches, and handsome tea-shaped flowers, which droop elegantly. The blossoms grow in every month of the year, but contain most oil in the months of June to December. The tree is common to many localities, but is found principally in well-populated districts, where it appears to thrive best. The reason for this has not been definitely ascertained, but it appears to be accurate and constant. It is propagated by planting seedlings or cuttings about 20 feet apart, which grow very rapidly, flowering in the third year.

“In Manila the petals are subjected to the simplest form of distillation, the oil being divided into two or more portions, the first clear and delightfully fragrant, the later distillate yellowish and frequently empyreumatic. It is stated that, to obtain a prime quality of essence, 300 to 350 lb. of flowers would be needed as to season and maturity of flowers to yield 1 lb. of the oil.

“The Java oil distillation has been described by De Jong after an official visit of inspection to Serang. The petals are stated to have been pounded before distillation, the resulting oil containing more sesquiterpenes, and being less fragrant than the Manila



oil. The methods of distillation have been much improved, with a corresponding improvement in the oil.

"In the distillation in Réunion no separation of the oil was made until recently, the idea being to obtain a high percentage yield rather than delicacy of odour, and, according to figures communicated to us, the yield is frequently as high as 2 per cent.

"The distinction between cananga oil and ylang-ylang oil is not sharply defined. The former usually consists of the higher fractions containing a greater proportion of sesquiterpene, but in some districts the entire oil is sold as cananga oil.

"Ylang-ylang oil is the finest grade, consisting of the first fractions of the oil, and containing a greater proportion of oxygenated constituents."

The cultivation of the tree reaches its maximum degree of perfection in the Philippine Islands, the finest oil being distilled in Manila. A considerable amount is also distilled in the island of Réunion, and a good deal of oil of less fine quality comes from Java and the neighbourhood. Commercially, the oil distilled in the Philippines is ylang-ylang oil *par excellence*. The oil from Réunion is usually termed ylang-ylang, but is not of such fine odour as the Manila oil; whilst the Java oil is known as cananga oil.

As there has been much confusion over this oil, the following account of it, due to R. F. Bacon (*Philipp. Jour. Sc.*, 3, 108, 65), will be of interest:—

In Manila, where the conveniences for careful distillation are greater than in outlying districts, fine oils as well as second-class oils—which are frequently known even there as cananga oil—are produced, but in the provinces the distillers, who are compelled to work with less scientific apparatus, generally produce only a second-class oil. Quite three-fourths of the blossoms delivered at Manila are green and unripe, although it is of the highest importance to use the ripe yellow blossoms for the best quantity and yield of oil. There has been much mystery made over alleged trade secrets connected with the distillation of this oil, but Bacon does not consider any such secrets exist. The great mistake distillers make in the provinces is burning the flowers in the still and wrongly selecting the fractions of the oil distilled. They attempt to get 1 kg. of oil from 150 to 200 kg. of flowers in one bulking, whereas they should only obtain 1 kg. of the finest oil from 400 kg. of flowers, and then about the same quality of second grade oil. The industry is also an important

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one in Réunion, and here again it has been shown that by a short-time distillation the smaller amount of oil is compensated by the fine quality.

Small quantities of the oil are produced in Madagascar and in the Seychelles Islands.

The climatic and soil conditions, coupled with the considerations above noted, account for the difference in the quality of the various oils. Bacon has examined a number of Philippine oils, and gives the following figures :—

	Second quality.	First quality.
Specific gravity at 30°/4° .	0.911–0.958	0.896–0.942
Refractive index at 30° .	1.4747–1.4940	1.4788–1.5082
Optical rotation . . .	– 27° to – 49.7°	– 27.4° to – 87°
Ester number . . . .	90–138 (in one case 169)	42–94

Bacon classifies the oils as follows. First-class oils usually have an ester number over 100, a refractive index not above 1.4900, and optical rotation rarely over – 45°. Low values for optical rotation and ester number usually indicate low-grade oils.

The usual analytical values for Réunion and Java oils are as follows :—

	Réunion.	Java.
Specific gravity at 15° .	0.930–0.967	0.906–0.956
Optical rotation . . .	– 34° to – 65°	– 15° to – 52°
Ester number . . . .	96 to 160	10 to 60
Refractive index at 20° .	1.5000 to 1.5100	1.4900 to 1.5050

Artificial ylang-ylang oil is a commercial product. The principal bodies used in its preparation are *para*-cresol methyl ether, linalol, geraniol, isoeugenol, benzyl acetate, benzyl benzoate, isoeugenol methyl ether, methyl benzoate, benzyl alcohol, and methyl anthranilate.

Adulteration of ylang-ylang or cananga oils with benzyl benzoate is a question of considerable difficulty to the analyst, as benzyl benzoate is, in certain proportions, a natural constituent of the oil. J. C. Umney (*P. & E. O. R.*, 1914, 37–85) gives the

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following figures for a number of samples of various origins which he examined :—

	Manila.	Bourbon.
Specific gravity . . .	0.927–0.969	0.964–0.967
Optical rotation . . .	— 38° to — 51°	— 39° to — 41°
Refractive index . . .	1.494–1.505	1.5130
Ester number . . .	99–153	143–160
Non-volatile residue (on water bath, in 2 hours) .	4.3–16.4 per cent.	25.1–40.3 per cent.

	Madagascar.	Mayotte.
Specific gravity . . .	0.961–0.981	0.947
Optical rotation . . .	— 30° to — 42°	— 48°
Refractive index . . .	1.5112	1.5007
Ester number . . .	123–171	115
Non-volatile residue (on water bath, in 2 hours) .	16.9–29.3 per cent.	14–19 per cent.

If, however, the oil is heated on a water bath until no further loss in weight is noted, any non-volatile residue over 7 per cent. should be regarded with suspicion. Further, the non-volatile residue should be saponified, and if the saponification value varies outside the limits 65 to 100, the oil is probably adulterated. If fatty oils have been used as adulterants, the saponification value will be much higher, and the residue must be examined for fatty acids, which can be separated and their molecular weight determined, which will indicate the origin of the adulterant.

Umney found that in the case of the finest Manila oils the residue does not usually exceed 6 per cent., although inferior oils contain more than this. The evaporation on the water bath should be continued for at least eighteen hours, as benzyl benzoate is very slowly volatilised at water-bath temperature.

*Roure-Bertrand Fils (Bulletin, April, 1910, 61)* give the table on p. 124 as typical figures for various ylang-ylang oils.

The following references are to important papers on the oil, where further details may be found :—

(1) "East African Ylang-Ylang Oil" (*Schimmel's Report*, October, 1911, 102).

	Réunion.	Nossi-Bé.	Mayotte.	Manila.
Specific gravity at 15° C.	0.9492	0.9673	0.9324	{ 0.911 to 0.958
Rotatory power	— 38° 8'	— 42° 12'	— 47° 40'	{ — 27° to — 49.7°
Solubility in 90 per cent. alcohol	{ ½ vol., then cloudy.	{ 1 vol., then cloudy.	{ 1 vol., then cloudy.	{ —
Acid value	—	1.4	1.0	—
Saponification value	96.03	129.5	113.4	90 to 138
Esters, as linalyl acetate	{ 33.6 per cent.	{ 45.3 per cent.	{ 39.7 per cent.	{ —
Saponification value of the acetylated oil	{ 132.11	{ 154.7	{ 134.4	{ —
Total alcohols (as linalol)	{ 40.3 per cent.	{ 42.7 per cent.	{ 41.0 per cent.	{ —
Combined alcohols	{ 26.4 per cent.	{ 35.6 per cent.	{ 31.2 per cent.	{ 24.7 to 38 per cent.
Free alcohols	{ 13.9 per cent.	{ 7.1 per cent.	{ 9.8 per cent.	{ —

(2) "Réunion, Nossi-Bé, Mayotte, and Manila Oils" (*Roure-Bertrand Fils, Bulletin*, April, 1910, 61, and October, 1911, 40).

(3) "Seychelles Ylang-Ylang Oil" (*Bulletin of the Imperial Institute*, per "The Chemistry of Essential Oils" (E. J. Parry), 4th ed., vol. i., p. 520).

**CANARIUM RESINS.**—There are a number of resins or oleoresins known under the name elemi. Most of these are the product of *Canarium* species, but the resinous matter most commonly known as elemi is the substance collected in the Philippine Islands, principally from *Canarium luzonicum*, and possibly from *C. commune*. This is known in commerce as Manila elemi. It contains from 15 to 30 per cent. of essential oil of some perfume value. The oleoresin is used as a fixative, but should be used in the form of an alcoholic tincture from which the insoluble matter has been rejected by filtration. When fresh, Manila elemi is pale yellow in colour, soft and granular, somewhat resembling crystallised honey in appearance. The general characters of the oleoresin vary with the district in which it has been produced, the soft and hard varieties having the following characters:—

	Soft.		Hard.
Volatile oil	15-30 per cent.	..	8-9 per cent.
Ash	0.02-0.2	..	0.2-1
Acid value	17-25	..	15-28
Ester value	7-25	..	25-28

The essential oil is a fragrant liquid recalling the odour of mace, and having the following characters: specific gravity, 0.870 to 0.915; optical rotation,  $+30^{\circ}$  to  $+55^{\circ}$ , but rarely  $+4^{\circ}$  to  $+134^{\circ}$ ; refractive index, 1.4775 to 1.4900; acid value, 0 to 2; and ester value, 4 to 10. The oil is very variable in composition. The following constituents have been detected in twenty-one samples examined by Clover (*Amer. Chem. Jour.*, 1908, 39, 613): limonene, phellandrene, pinene, terpinene, and terpinolene. A sesquiterpene alcohol, elemol (*q.v.*), is also present, and a small amount of a phenol ether which has been named elemicin.

**CARAWAY OIL.**—This oil is obtained by the distillation of caraway fruits, the product of *Carum carui*, a plant found in northern and central Europe. It is cultivated in various countries, especially in Holland. The name caraway and the Spanish name *alcarahueya* are derived from the Arab *karawya*. The fruits yield from 3 to 7 per cent. of essential oil having the following characters: specific gravity, 0.907 to 0.918; optical rotation,  $+70^{\circ}$  to  $+83^{\circ}$ ; refractive index, 1.4840 to 1.4890; and containing 50 to 60 per cent. of carvone.

Caraway oil consists almost entirely of carvone (carvol),  $C_{10}H_{14}O$ , and the terpene limonene. Its value depends on the carvone, so that it may be approximately valued by its specific gravity, that of carvone being 0.964, and that of limonene 0.848.

The best method for the determination of carvone is the neutral sulphite method (*vide* "Aldehydes, Determination of"). If the oil be fractionally distilled, not more than about 25 per cent. should distil below  $180^{\circ}$ , and from 55 to 65 per cent. should distil above  $200^{\circ}$ .

On the Continent pure carvone is largely employed in place of caraway oil. Hence there is a considerable amount of caraway oil available from which much of the carvone has been abstracted. Some of these oils are standardised to the lowest limits that the various pharmacopœias give for the oil; others have so much carvone abstracted that they can only be sold as "light" caraway oil or, in common with the oil distilled from the chaff and dust left after threshing the seed, as "caraway chaff" oil. These light oils are employed in cheap soap perfumery. A still lower grade oil is sometimes sold under the name "carvene." This is merely impure limonene with a slight caraway odour, and consists substantially of the terpenes of caraway oil.

**CARDAMOM OIL.**—Traces of cardamom oil are sometimes used in eau de Cologne and in artificial lily perfumes. The

ordinary cardamom is the fruit of *Elettaria cardamomum*, one of the *Zingiberaceæ*. Although the plant grows wild in the forests of southern India, where it is commonly known as *kachi*, the bulk of the fruits of commerce are provided by cultivated plants, and Ceylon supplies the greater part of the cardamoms used. Some of the cardamoms met with are the product of one or more varieties of the plant, and yield essential oils which differ between themselves. The writer (E. J. P.) has distilled the oil from the so-called Ceylon-Malabar and the Ceylon-Mysore seeds. The former yielded 1.3 per cent., and the latter 2.6 per cent., of essential oil. The odours of the two oils were practically indistinguishable. The following figures cover those of most pure samples: specific gravity, 0.923 to 0.945; optical rotation,  $+24^{\circ}$  to  $+48^{\circ}$ ; refractive index, 1.4620 to 1.4675; and ester value, 90 to 150.

The oil contains terpinyl acetate, terpineol, and limonene. (See also E. J. Parry, "The Chemistry of Essential Oils," 4th ed., vol. i., p. 101; Sawyer's "Odorographia," 2nd series, p. 111; and Ridley, "Spices," p. 324.)

**CARNATION.**—The carnation is merely a variety of the clove pink *Dianthus caryophyllus*, the species including carnations, pinks and picotees. The rich odour of the less highly cultivated varieties of the clove and carnation has always been exceedingly popular. In the more highly cultivated flowers perfume has given way to form and colour, as in the case of the rose. A certain amount of the natural perfume is extracted in the south of France, principally in the form of a pomade, although a little concrete or absolute reaches the market. The bulk of the carnation perfume, however, is based on synthetics, rounded off with natural flower perfumes and fixatives. According to a writer (anonymous) in the *Perfumery and Essential Oil Record*, 1917, 18, nearly all the species of *Dianthus* are natives of Europe, tropical Asia, and northern Africa. In France, where it is known as *Œillet*, it is largely cultivated for decorative purposes. It is a beautiful plant, remarkable not only for its perfume, but for the colour and elegance of its flowers. Some 2,000 varieties have been produced by cultivation, of which the following may be mentioned: Alégatière (vivid red flowers), Antoine Devert (cerise coloured), Commandant Rivière, Comtesse de Paris (yellow), François Büchner (bright red), General Boulanger (vivid red), Hugues (abundant red flowers), Jean Sisley (red and yellow), La Fontaine (yellow, striated), Léon Aurange (bright cerise), Madeleine Solignac (lilac rose), Mahonais (flesh coloured, flourishing in winter and

early spring, cultivated round Toulon), *Enfant de Nice* (red or white flowers), *Pauline Borriglione* (rose or salmon pink), *Président Carnot* (purple flowers), *Rose Rivoire* (rose coloured), *Souvenir de Ffine Mari* (white flowers), and *Souvenir de Madame Gobet* (yellowish copper coloured).

Other varieties which flourish in winter are *Auguste Vernier*, *Capitaine Berner*, *Laverrière*, *Madame de Presle*, *Oriflamme*, *Raphael*, and *Roi des Rouges*.

*Cultivation*.—Carnations flourish best in a well-drained soil with free access of air and sheltered from the sun. They are reared from seed, and from layers or suckers. Seeds are sown in autumn or spring in earthenware pans or pots. When sown from March to May, the young plants may be planted out about fourteen months afterwards, when they possess five or six leaves, care being taken to protect them from the sun's rays and from cold and damp. To obtain autumn or winter flowers, the seeds are sown in autumn. Slips should be planted in a light sandy soil in pots, leafy branches being preferable for this operation. The slips will root in thirty to forty days. Layering is effected by embedding the branches near a node, after making a small longitudinal incision before burying them. This favours the development of roots. The branches are kept in place by means of small pieces of wood. During the summer the extremities of branches which tend to lengthen are pinched, in order to render the plant more vigorous and retard flowering. From time to time liquid manure should be applied to obtain a greater abundance of flowers.

A clove-scented perfume is also developed in the flowers of a convolvulus found in the forests of Mednapore, in Bengal, which is botanically known as *Lettsonia bona-nox* (Roxburgh). The flowers are large and white, expanding at sunset and withering at sunrise; they are produced during the rainy season.

Another clove-scented convolvulus is the *Ipomœa grandiflora* (Roxburgh), known in Bengal as *Doodiya-Kulmi*. This plant twines to a height of 20 feet, and bears white flowers 4 to 6 inches in diameter. It is common in hedges in Samulcota and on the banks of watercourses. It is closely allied to the *Lettsonia bona-nox*.

A clove odour is strongly developed in the bark of *Laurus culilawan* (*Laurus Carophyllata*), and in *Cinnamomum sintox*. The bark of *Cinnamomum culilawan*, a native of Amboyna, is called "clove bark" on account of its strong odour of cloves. "Clove cassia" is the name applied to the bark of *Dicypellium Caryophyl-*

*latum*, which is also known as Brazilian clove bark. It is found in Para and Rio Negro. The Madagascar clove nutmeg is the fruit of *Agathophyllum aromaticum*, a laurel the leaves of which are used by the natives as a condiment.

The actual basic material for artificial carnation is isoeugenol (*q.v.*), usually mixed with some eugenol. Hexyl-methyl ketone, isobutyl-phenyl acetate, benzyl acetate, phenyl-acetic aldehyde, and terpineol are also often employed in judiciously small amount, with a little benzyl isoeugenol as a useful fixative. A useful variation in "shade" of the odour is produced by the use of a little methyl eugenol and methyl isoeugenol.

The essential oil of the carnation has recently been examined by Glichitch (*Bull. Soc. Chim.*, 1924, iv., 35, 205). The yield is only about 0.003 per cent. calculated on the fresh flowers. The oil is a pale green solid of intense odour, which, until heavily diluted, does not resemble the odour of the flower. It melts at 35° to 37°, and has a specific gravity 0.869 at 40°; optical rotation,  $-8^{\circ} 28'$ ; acid number, 4.9; ester number, 61.3. It contains 31 per cent. of a stearoptene, which is probably heptacosane,  $C_{27}H_{56}$ , melting at 53° to 54°. Traces of an aldehyde are also present.

**CARROT, OIL OF.**—See "Daucus, Oil of."

**CARVACROL.**—This body is a phenol, of the formula  $C_{10}H_{14}O$ , isomeric with thymol. Chemically it is isopropyl-*ortho*-cresol. It is found, frequently in association with thymol, in various thyme and origanum oils. It also results artificially from the treatment of carvone by potash. It is a colourless oil of fragrant, refreshing odour, solidifying at about 1°, boiling at 236°, of specific gravity 0.981, and refractive index 1.5240.

**CARVENE.**—See "Caraway Oil."

**CARVONE.**—Carvone,  $C_{10}H_{14}O$ , is a ketone, the characteristic odour bearer in oils of caraway and dill, in which it occurs as *dextro*-carvone. It is found as *laevo*-carvone in kuromoji oil. It is an odorous liquid of specific gravity 0.964; optical rotation,  $+59^{\circ} 30'$ ; refractive index, 1.5020; and boiling point, 224°.

**CARYOPHYLLENE.**—This body is a sesquiterpene,  $C_{15}H_{24}$ , occurring in oil of cloves and several other essential oils. There are several isomeric bodies known under this name which are of considerable interest to the chemist. But from the perfumer's point of view the mixture of sesquiterpenes obtained from oil



of cloves when the eugenol has been almost completely extracted is known as caryophyllene. This mixture has a specific gravity from 0.905 to 0.910; optical rotation,  $-7^{\circ}$  to  $-9^{\circ}$ ; refractive index, about 1.5010; and boiling point, about  $258^{\circ}$  to  $261^{\circ}$ . With a little eugenol left in the mixture, it is the "light" clove oil sold for cheap soap perfumery.

**CASCARILLA.**—The cascarilla bark of commerce is the bark of *Croton Eleuteria*, and possibly that of *Croton Cascarilla*. The trees are indigenous to the Bahama Islands. The bark has a pleasant aromatic odour and burns with an exceedingly fine fragrance, so that it is often used in fumigating or incense compositions. It yields from 1 to 3 per cent. of essential oil, which is occasionally used in perfumery, and which has the following characters: specific gravity, 0.895 to 0.928; optical rotation,  $+1^{\circ}$  to  $+12^{\circ}$ ; refractive index, 1.4910 to 1.4960; and ester number, 65 to 75. The perfume constituents have not been identified, but it contains a sesquiterpene alcohol,  $C_{15}H_{24}O$ , and an acid isomeric with undecylenic acid.

**CASSIA OIL.**—Cassia oil is the distillate from the leaves, twigs, and other portions of *Cinnamomum cassia*, the so-called Chinese cinnamon, which is probably a native of Cochin China. It is chiefly cultivated in China proper, the three principal districts being Taiwu in the Kwangsi province, Lupko, and Loting in the Kwangtung province. In a report on a journey to Kwangsi by H. Schroeter in 1897, the writer stated that the shrubs destined for the production of the *Cassia lignea*, as the prepared bark is termed, are partly stripped during the summer months of their smaller branches and their juicy leaves. These are then boiled in large vessels, and the cassia oil recovered by a primitive system of distillation. An interesting account of the origin of the oil is contained in a paper in the *Journal of the Linnean Society*, December, 1882. The distilleries are situated in valleys where an abundant flow of water for condensing purposes is available. If leaves only are used for distillation, the oil is of the finest quality, so that, as a rule, only about 30 per cent. of twigs are used with 70 per cent. of leaves. A typical oil so distilled was found by Niedhardt to contain 86 per cent. of cinnamic aldehyde, the principal odorous constituent of the oil. A specimen distilled entirely from the bud sticks was found by Schimmel & Co. to contain 92 per cent. of cinnamic aldehyde, and the following results were obtained from various parts of the plant: (1) Cassia

bark : yield, 1.5 per cent. ; specific gravity, 1.035 ; cinnamic aldehyde in the oil, 89 per cent. (2) Cassia buds : yield, 1.55 per cent. ; specific gravity, 1.026 ; cinnamic aldehyde in the oil, 80.4 per cent. (3) Cassia bud sticks : yield, 1.64 per cent. ; specific gravity, 1.046 ; cinnamic aldehyde in the oil, 92 per cent. (4) Cassia leaves, stalks, and twigs : yield, 0.77 per cent. ; specific gravity, 1.055 ; cinnamic aldehyde in the oil, 93 per cent.

Cassia oil is imported chiefly from Hong Kong in "leads"—leaden vessels holding  $16\frac{2}{3}$  lb. of the oil. It is invariably sold graded on its cinnamic aldehyde content, viz., 70 to 75 per cent., 75 to 80 per cent., 80 to 85 per cent., and 85 to 90 per cent., the usual quality being 75 to 80 per cent. The lower grades are almost invariably adulterated, usually with rosin, pure oils rarely containing less than 85 per cent. of cinnamic aldehyde. A pure oil (*i.e.*, as distinguished from the oils which may be said to be standardised down more or less honestly) has the following characters :—

Specific gravity	.	.	.	1.055–1.072
Refractive index	.	.	.	1.6000–1.6060
Optical rotation	.	.	.	– 1° to + 6°
Acid value	.	.	.	6–20
Cinnamic aldehyde	.	.	.	Not below 83 per cent.

A pure oil is soluble in 2 volumes of 80 per cent. alcohol. Nearly all adulterants interfere with this character. Ordinary rosin, or colophony, the most usual adulterant, can be detected, firstly, by a much increased acid value, as colophony consists almost entirely of resin acids or anhydrides ; secondly, by adding a few drops of a saturated alcoholic solution of acetate of lead to a 25 per cent. solution of the oil in 70 per cent. alcohol. A distinct precipitate indicates the presence of rosin. An estimation of the amount of the adulterant is not usually necessary, as the determination of the cinnamic aldehyde, upon which the value of the oil practically entirely depends, is far more accurate than any rosin determination. It can, however, be approximately determined by heating the oil to 280°, until white fumes are given off, when any residue above 10 per cent. may be regarded as colophony. Cassia oil attacks the lead of the containers, owing to the presence of cinnamic and other acids. Lubetti (*Jour. Soc. Chem. Ind.*, 1920, 35) tests for this as follows : 5 c.c. of the oil are dissolved in 15 c.c. of 90 per cent. alcohol, and this solution "Nesslerised" against a standard solution of lead acetate in alcohol, with

sulphide of ammonium, using a lead-free cassia oil (redistilled) in the blank solution. (For the estimation of the cinnamic aldehyde (*q.v.*), see under "Aldehydes, Determination of.")

Cassia oil closely resembles cinnamon oil in odour, but it is not nearly so delicate. Apart from cinnamic aldehyde, the oil contains a little cinnamic acid, terpenes, the acetic esters of cinnamic and phenyl-propyl alcohols, *ortho*-methyl-coumaric aldehyde, salicylic aldehyde, coumarin, and salicylic and benzoic acids.

Cassia oil is used in the perfuming of "old brown Windsor" soap, and in many perfumes where a less delicate odour than that of the finer cinnamon oil is permissible. Both oils are frequently replaced by artificial cinnamic aldehyde.

CASSIE.—See "Acacia."

CASTOR, or castoreum, is an animal perfume material of considerable value to the perfumer as a fixative. It consists of the dried membranous follicles of the beaver (*Castor fiber*), which are situated between the anus and genital organs of the animal of both sexes. They are filled with a viscid oleoresinous glandular secretion, which is of disagreeable odour, but which is not noticed on dilution. The follicles are removed after the animal is killed, and dried either by smoke or in the sun. When quite fresh, castor is a white creamy liquid, but by the time it appears in commerce it is unctuous and semi-solid. Two varieties are recognised, the Canadian and the Russian, the latter, however, rarely reaching this market. Castor is sold in the form of more or less soft and unctuous masses which gradually harden, and which are contained in flattened and wrinkled sacs from 2 to 3 inches long. It is nauseous as to odour, and of a bitter taste. So far as London is concerned, castor comes on to the open market only once a year, as it is almost a monopoly of the Hudson's Bay Company, who offer the year's collection at an annual sale, the amount offered being about 1,000 lb.

In addition to its direct use as a fixative, castoreum frequently enters into the composition of the so-called artificial "ambers."

Castor varies considerably in composition, always, however, containing a small quantity of a highly odorous essential oil. It contains from 40 to 70 per cent. of resinous matter soluble in alcohol, traces of salicin and benzoic acid, and from 4 to 5 per cent. of a crystalline body which has been named castorin. According to Mingard, castor contains 88 per cent. of matter soluble in ether, and about 8 per cent. of substances volatile at

100°. Castor has frequently been described erroneously as the dried testicles of the beaver.

**CEANOTHUS VELUTINUS, OIL OF.**—According to Lynn, Lee, and Clausen (*Jour. Amer. Pharm. Ass.*, 1923, 12, 419), the leaves of this plant, known in the United States as the sticky laurel, or mountain balm, yield about 0.1 per cent. of essential oil having a specific gravity 1.0157 at 25°, and refractive index 1.5315 at 20°. It is optically inactive. It contains cinnamic aldehyde, and probably eugenol. It has a sweet odour resembling cinnamon and clove.

**CEDAR WOOD OIL.**—This essential oil is of considerable value, mostly for cheap perfumery where a heavy odour is required. It is distilled from the wood of *Juniperus virginiana*, the Virginia cedar, with, possibly, the admixture of other cedar woods. Much of it is distilled from the waste shavings obtained in the American lead pencil factories. The finely powdered wood burns with a highly aromatic odour, and is used in incense and similar preparations, and for ceremonial or fumigating purposes. Although a very inexpensive oil, it is useful in high-grade as well as cheap perfumery, and blends well with odours of the violet type. The pure oil has a specific gravity from 0.940 to 0.962, and optical rotation  $-25^{\circ}$  to  $-47^{\circ}$ . The refractive index varies from 1.5000 to 1.5100. The principal constituent of the oil is the sesquiterpene cedrene,  $C_{15}H_{24}$ ; it also contains cedrol, or "cedar camphor,"  $C_{15}H_{26}O$ , cedrenol,  $C_{15}H_{24}O$ , and *pseudo*-cedrol,  $C_{15}H_{26}O$ . Cedrol is a crystalline body of pleasant aromatic odour, melting at  $84^{\circ}$ .

The Atlas cedar (*Cedrus Atlantica*) is also distilled on a small scale for its oil. This tree is probably only a variety of the cedar of Lebanon (*Cedrus Libani*). The oil is similar to ordinary cedar wood oil, but of finer odour. It has a specific gravity 0.950 to 0.970; optical rotation,  $+45^{\circ}$  to  $+62^{\circ}$ ; and refractive index, 1.5119 to 1.5175.

Roberts (*Jour. Chem. Soc.*, 1916, 791) has examined the oil distilled from *Cedrus deodara*, the deodar tree, a native of the western Himalayas, which is widely distributed in northern India. The oil has a pleasant balsamic odour, and has the following characters: specific gravity, 0.955 to 0.976; optical rotation,  $+34^{\circ}$  to  $+52^{\circ}$ ; refractive index, 1.5195 to 1.5225; and ester number, 5 to 21. It contains a ketone, which is probably *para*-methyltetrahydroacetophenone. Deodar wood oil has recently

been examined by J. L. Simonsen, D.Sc., and M. G. Rau at the Forest Research Institute, Dehra Dun (*Indian Forest Records*, 1922, 9, 123). The oil employed by them was derived from logs seventy-five years old, which furnished a yield of 2·5 per cent. of oil.

The pleasant aromatic odour which characterises deodar oil was stated by Roberts to be probably due to the presence of from about 2 to 10 per cent. of *p*-methyltetrahydroacetophenone, a compound not found previously in nature. This statement has been confirmed by the above investigators, who worked with a large quantity of the oil, and were thus able to isolate the ketone in a pure condition, and establish its identity by preparing many of its derivatives.

The principal constituent of the oil is a sesquiterpene, which is associated with a sesquiterpene alcohol; as, however, neither of these compounds yielded a crystalline derivative, it was not possible to characterise them beyond determining their physical constants. Other constituents which have been isolated from deodar oil are as follows: a phenol (unidentified) and esters of butyric or isobutyric, hexoic, heptoic, and stearic acids.

Samples of deodar oil were submitted by the Imperial Institute in 1915 to English and Continental firms of soap makers and essential oil distillers, who expressed the general opinion that a market could probably be found for the oil if it were offered at a low price. It was stated concerning a sample of oil which the forest chemist has had valued recently in England, that the oil might find a small market as a substitute for cedar wood oil in soap perfumery, but that its value would only be 2s. 6d. per pound. At this price it was not considered that production would be remunerative.

The suggestion has now been made that it might possibly prove profitable to utilise the oil obtained by the destructive distillation of the wood as a timber preservative.

A cedar wood from East Africa, obtained from *Juniperus procera*, has been arriving in Europe for some time past. *Messrs. Schimmel & Co.* (*Bericht*, October, 1911, 110) distilled a certain quantity of the sawdust and boards of the African wood, and obtained the following results:—

	Sawdust.	Boards.
Yield of essential oil . . .	3·2 per cent. . .	3·24 per cent.
Specific gravity at 15° . . .	0·9876 . .	1·0289
Refractive index . . .	1·50893 . .	1·51011
Optical rotation . . .	—37° 10' . .	—32° 30'

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	Sawdust.	Boards.
Acid value . . . . .	14.9	27.06
Ester value . . . . .	8.4	7.93
Ester value after acetylation . .	70.0	89.6
Solubility in 80 per cent. alcohol	1.6 vol.	2 vols.
Solubility in 90 per cent. alcohol	0.5 vol.	0.5 vol.

**CEDRAT OIL.** (See "Citron Oil.")—The cedrat oil of commerce is almost invariably a mixture of lemon with other *Citrus* oils. The French "oil of cédrat" is, when pure, citron oil, an oil closely resembling lemon oil, having a specific gravity from 0.850 to 0.855; optical rotation,  $+77^{\circ}$  to  $+83^{\circ}$ ; and refractive index about 1.4750. It contains citral and terpenes. The French "oil of citron" is oil of lemon.

**CEDRELA WOOD.**—Cedrela wood must not be confused with cedar wood, although its similar odour often causes it to be so confused. *Cedrela odorata* is a native of the Caribbee Islands and the Barbadoes. It grows to an immense size in Jamaica. The wood has a pleasant cedar-like odour, hence it is often called Jamaica or Honduras cedar. Cigar boxes are usually made from this wood. It yields up to 1 per cent. of a fragrant essential oil having a specific gravity 0.923 to 0.950, and refractive index 1.5040. Similar oils are obtained from the La Plata, Punta Arenas, and Corinto cedar or cedrela trees. (See E. J. Parry, "The Chemistry of Essential Oils," 4th ed., vol. i., p. 494.)

**CELERY, OIL OF.**—The seeds of the common celery, *Apium graveolens*, yield about 3 per cent. of essential oil, which, when distilled from the cultivated plant, is of considerable value to the perfumer, both as a fixative and as an addition to floral perfumes, such as sweet pea, etc. The oil has a specific gravity 0.860 to 0.895; optical rotation,  $+40^{\circ}$  to  $+82^{\circ}$ ; and refractive index, 1.4780 to 1.4860. It owes its odour almost entirely to the lactone sedanolide,  $C_{12}H_{18}O_2$ . The oil has been critically examined by Ciamician and Silber (*Berichte*, 1897, 30, 492, 1419).

**CETACEUM.**—Cetaceum or spermaceti is a solid wax obtained from the head of the sperm whale, *Physeter macrocephalus*, and other allied sea mammalia. It is deposited from the sperm oil found in the head of these whales, and is purified by filtration, re-melting and treatment with dilute alkali. It has the following characters: specific gravity, 0.945 to 0.960; acid value, not exceeding 1; saponification value, 125 to 138; iodine value, 3 to 5; melting point,  $43^{\circ}$  to  $50^{\circ}$ ; and refractive index about

1.4330 at 80°. It consists principally of cetyl palmitate. Adulteration with stearic or other fatty acids is indicated by a high acid value, and, if paraffin wax is present, the sample will not dissolve clearly in 50 to 60 parts of boiling alcohol. Spermaceti is used to a considerable extent in the preparation of creams and lip salves.

**CHA HWA.**—This plant, a species of *Camellia*, is very similar to the tea plant, hence its name of “cha hwa,” or tea flower. It is largely found in the wild state, flourishing on the slopes and summits of the mountains in the province of Che Kiang. The chief utility of tea flower lies in its employment as a scent for imparting aroma to the best quality of China tea. Often the petals, as well as the entire flowers, are mixed with the tea to increase its fragrance, and the resulting mixture, infused in the picturesque Chinese teacups, gives a particularly pleasant beverage. This plant also yields a nut, the size of an arachis nut, having a brownish colour. These nuts, when subjected to expression, yield a light brown oil, which has a somewhat aromatic odour. The oil is known locally as *Cha You*, or tea oil, and finds extensive use in the coiffure of Chinese ladies. Its cultivation is encouraged on this account, and it is especially valuable, being easily grown in situations suitable for little else.

**CHAMPACA FLOWER OIL.**—This beautiful perfume has no relationship with the so-called champaca wood oil (*q.v.*). It is distilled from the flowers of *Michelia champaca*, probably usually mixed with the flowers of *Michelia longifolia*. The former yields yellow, and the latter white, flowers. The plants are natives of India, and the oil is known to the natives as *pand* or *champa-kautter* and other names. It is, in India, found principally in Nepaul, Assam, and Bengal. It is also cultivated in the Philippine Islands. The perfume of the flowers is exquisite, but almost overpowering. The native Indian women adorn their hair with the flowers for the sake of the perfume and for the rich yellow-orange colour, which contrasts so well with their black hair. The tree is highly venerated by the Hindus, who have given one of its names, *Tulasi*, to a sacred grove on the banks of the Yamuna. It is also dedicated to the god Vishnu.

The following account is due to *Roure-Bertrand Fils* (*Bulletin*, April, 1909, 24):—

“The tree is known by different names according to the district: *Champaca*, *Champak* in Bengal, *Tita-sapa* in Assam, *Oulia Champ*. in Nepaul; it is also known in other parts of the

country under the names of *Shampang*, *Shimbu*, *Sempangam*, *Sampige*, *Champakam*, *Saga*, *Sapu*, etc. This large tree, which is an evergreen, prefers sandy soils. It is of fairly large size, since a man can scarcely encircle the trunk with his arms. This trunk is grey on the outside, and under the thick and greenish-coloured bark the wood is nearly white. The branches present the same external appearance. The leaves are not very close together; they have long petioles, are oblong in shape, stiff, greenish brown, brilliant above, paler underneath. The nerves are prominent on the under-face.

"The flowers, of a yellow colour, are produced at the tops of the branches, and are carried by stout peduncles of a yellowish green colour, polished and erect. The number of flower heads may vary slightly; in general there are eight heads to the verticillaster. The sepals are rounded at their extremities, the petals are cuspidate. The stamens are numerous, the style is short and stout. The fruits are on spikes or in bunches, round, oblong, pale yellow when ripe. They contain numerous seeds, rounded on one face, flattened on the others owing to their reciprocal pressure in the fruit.

"There are two flowerings annually, and the tree only yields fruits after some years.

"According to our personal observations, the perfume of the flowers of the Philippine champaca is stronger and sweeter than that of the Singapore, Penang, Colombo and Peradeniya flowers. It would appear that it is the same with this tree as with the ylang, which does not yield the same essential oil in Java, the Straits or Ceylon as in the Philippines. It is said that in India the seeds of the champaca are yellow, whilst in the Philippines they are cherry red.

"The yellow colouring matter of the flowers is utilised in dyeing. The seeds yield a fatty oil by pressing; the flowers contain a volatile oil, and yield, on distillation, a very pleasant aromatic water. All parts of the plant possess a strongly spiced flavour."

*Michelia champaca* is generally cultivated, but is found wild over a large area. Cultivation greatly improves the perfume. The oil has a specific gravity from 0.883 to 0.897, optical rotation about  $-13^{\circ}$ , refractive index about 1.4470 at  $30^{\circ}$ , and ester number about 180. It contains benzyl alcohol, linalol, geraniol, esters of methyl-ethyl acetic acid, methyl anthranilate, iso-eugenol, benzoic acid, methyl-eugenol, and a crystalline body of the formula  $C_{16}H_{20}O_5$ , melting at  $166^{\circ}$ . Oil distilled in Manila



was found by Brooks (*Philipp. Jour. Sc.*, 1911, 6, 333) to have a specific gravity at 30°/30° between 0.904 and 0.9107; refractive index, 1.4640 to 1.4688; and ester number, 124 to 146. An oil distilled in the Malay Peninsula had a specific gravity 0.922; optical rotation, + 12° 30'; and ester number, 15.2. This oil has little odour value. There are several other odorous species of *Michelia*, but they are not used for distillation purposes. Champaca odour is heavy and persistent, of the same type as ylang-ylang and the larger varieties of perfumed lilies.

**CHAMPACA WOOD OIL.**—See "*Bulnesia sarmienti*."

**CHAMPACOL.**—This body is a crystalline alcohol present in the oil of *Bulnesia sarmienti* (*q.v.*). It has been examined by Wallach and Tuttle (*Annalen*, 1894, 279, 395). It has the formula  $C_{15}H_{26}O$ , and was first named champacol by Merck, when it was believed that the wood was true champaca wood, but has been renamed guaiol. It is a crystalline body melting at 91°, and boils at 288°. It has a tea rose odour.

**CHASSIS.**—The name given to the wooden frames, usually with glass bottoms, upon which flowers are treated with fat for the extraction of their perfume in the process known as enfleurage (*q.v.*).

**CHAVIBETOL.**—This body, also known as betel-phenol, has the formula  $C_{10}H_{12}O_2$ . Chemically it is an allyl-guaiacol, boiling at 255°, of specific gravity 1.069; refractive index, 1.5413; and optical rotation, + 8.5°.

**CHAVICOL.**—This body,  $C_9H_{10}O$ , is a phenol occurring in bay and betle oils. It is a highly odorous liquid, of specific gravity 1.035; refractive index, 1.5441; optical rotation, 0°; and boiling point, 237°. Chemically it is *para*-oxyallylbenzene.

**CHEIRANTHUS CHEIRI.**—This plant is the wallflower, or in France *giroflée*. It is a perennial plant of the natural order *Cruciferae*, indigenous to southern Europe. The flowers yield a mere trace of essential oil, so that the natural perfume is not a commercial article. Kummert (*Chem. Zeit.*, 1911, 667) has made an exhaustive examination of the oil obtained, to the extent of 0.06 per cent., by extracting the flowers with a volatile solvent and distilling the oil. He found it to have a specific gravity 1.001, and a saponification value 20.35. He found present nerol, geraniol, linalol, benzyl alcohol, indol, methyl anthranilate, esters of salicylic acid, a *para*-cresol compound, a lactone, and probably irone and anisaldehyde. An artificial perfume named cheiranthin

is compounded on the basis of the above details, and probably also contains isoeugenol and isobutyl-phenyl acetate. Hydroxy-citronellal and *para*-cresol methyl ether are also employed, especially the latter.

**CHEVREFEUILLE.**—A name for honeysuckle perfume (*q.v.*).

**CHLOROSTYROL.**—Styrolene (phenyl-ethylene),  $C_8H_8$ , yields two sets of halogen derivatives, of which the  $\alpha$  derivatives are useless in perfumery, but the  $\omega$  derivatives have a powerful hyacinth odour.  $\omega$ -Chlorostyrolene,  $C_6H_5CH : CHCl$ , is obtained by the action of caustic alkali on dichlor-ethyl benzene. Its odour, however, is not so fine as  $\omega$ -bromostyrolol (*vide* "Bromostyrol"). It boils at  $198^\circ$  to  $199^\circ$ .

**CHRYSANTHEMUM OILS.**—*Chrysanthemum marginatum* (natural order *Compositæ*) is a plant indigenous to Japan, where it is known as *Isokiku*. According to Shinosaki (*Jour. Chem. Ind. Tokyo*, 1919, 22, 455) it yields 0.005 per cent. of essential oil, of a greenish blue colour, having the following characters:—

Specific gravity	. . . . .	0.9231
Optical rotation	. . . . .	— $47^\circ$
Refractive index	. . . . .	1.5020
Saponification value	. . . . .	16.3
Saponification value after acetylation	. . . . .	63

The oil is aromatic, but its constituents have not definitely been identified. This oil may be identical with that described by Perrier (*Bull. Soc. Chim.*, 1900, iii., 23, 216) under the name *kiku* oil, from *Chrysanthemum Japonicum*, although the characters of the two oils are different. The flowers of *Chrysanthemum cinerariæ-folium*, which provide the insect powders of commerce, yield an essential oil with a powerful odour. Its constituents have not been completely investigated (Siedler, *Berichte Deutsch. Pharm. Ges.*, 1915, 25, 297).

**CHYPRE.**—This name is a fancy one, which has become of very common application in the perfume industry. It is a perfume of heavy odour, which is usually based on musk, verbenæ and sandalwood with a little sassafras oil or safrol, with *mousse de chêne* or benzoin as a fixative. Clary sage oil is also frequently present, and often a little bergamot oil.

**CINEOL.**—See "Eucalyptol."

**CINNAMIC ACID.**—Cinnamic acid,  $C_6H_5.CH : CH.CO_2H$ , is found, both in the free state and in the form of esters, in various

essential oils, especially those of balsamic substances such as storax. It is a crystalline body, melting at  $133^{\circ}$ , and boiling at  $300^{\circ}$ . It has a pleasant odour and is useful as a fixative, as the odour is not too pronounced. It is prepared artificially by heating 2 parts of benzaldehyde and 3 parts of acetic anhydride with 1 part of fused sodium acetate, to  $180^{\circ}$  for twelve hours. The reaction mass is extracted with water, and the cinnamic acid precipitated from the aqueous solution by hydrochloric acid. It is also prepared on an industrial scale by heating benzylidene chloride with fused sodium acetate to  $200^{\circ}$ .

Claisen (*Berichte*, 1890, 978) prepares it by treating ethyl acetate and sodium with benzoic aldehyde at ice temperature. (See also the various cinnamyl esters.)

Synthetic cinnamic acid is a mixture of two isomeric acids. It is composed of an acid identical with the natural acid ( $\alpha$ -cinnamic acid) and  $\alpha$ -heterocinnamic acid.

$\alpha$ -Heterocinnamic acid may exist in two forms. In a recent paper (*Berichte*, 42, 2649, 2655), Erlenmeyer has undertaken a study of the conditions of formation of these various isomerides in nature, and also of the synthetic cinnamic acids, prepared according to the different known methods. These modes of formation, which are very numerous, are summarised in a table attached to the paper, to which the reader is referred.

Erlenmeyer first shows that heterocinnamic acid exists, although in very small proportions, in the natural cinnamic acid extracted from styrax benzoin.

It appears to follow, from a critical examination of the synthetic methods which make use of benzaldehyde as their starting point, that, to a large extent, the variations observed in the properties of the cinnamic acids obtained should be attributed to the influence of impurities in the raw material.

Thus, natural benzaldehyde, which always contains a certain quantity of hydrocyanic acid, and which gives rise mainly to  $\alpha$ -cinnamic acid when treated according to Perkin's method, behaves, after all the hydrocyanic acid has been eliminated, like the synthetic aldehyde, which yields, under the same treatment, storacic acid and the  $\alpha$  and  $\beta$  modifications of heterocinnamic acid. (See also Campbell and Sudborough, *Jour. Chem. Soc.*, 95, 1538; Liebermann and Trücksass, *Berichte*, 42, 4659, 43, 411; and Riber and Goldschmidt, *Berichte*, 43, 453.)

**CINNAMIC ALCOHOL.**—This substance, of the formula  $C_6H_5.CH:CH.CH_2OH$ , is also known as styrene. It exists,

principally in the form of its acetic and cinnamic esters, in storax, balsam of Peru, and in hyacinth and other floral oils. Much of the commercial substance is prepared by the hydrolysis of the cinnamic esters present in storax. It is prepared artificially by reducing cinnamic aldehyde diacetate by means of iron and acetic acid, and saponifying the resulting esters. It is a crystalline body, melting at  $30^{\circ}$  to  $33^{\circ}$ , but commercial specimens almost invariably contain traces of impurities which keep it in a liquid condition. It has a specific gravity about 1.020 (commercial specimens vary from 1.015 to 1.030); refractive index, 1.5720 at  $30^{\circ}$ ; and boiling point,  $258^{\circ}$ . The odour of cinnamic alcohol is weak, but very sweet and delicate. It is useful in the preparation of artificial hyacinth and similar floral odours.

**CINNAMIC ALDEHYDE.**—This aldehyde is the principal odorous constituent of cinnamon and cassia oils. Its formula is  $C_6H_5.CH : CH.CHO$ . It can be extracted from the oils in which it occurs by shaking it with a hot solution of sodium bisulphite, which combines with the aldehyde to form a soluble compound. The aqueous solution is separated from the non-aldehydic constituents, which float on the surface of the liquid as an oil, and on the addition of dilute sulphuric acid the aldehyde is liberated from the bisulphite compound, and can be distilled in a current of steam.

Cinnamic aldehyde is prepared on a comparatively large scale by condensing benzaldehyde with acetic aldehyde in the presence of an alkali. This method, originally due to Boehringer (German Patent 19018), is as follows: A solution of 5 parts of benzaldehyde and 5 parts of acetic aldehyde in 10 parts of alcohol is cooled to  $10^{\circ}$ , and 10 parts of a 25 per cent. solution of caustic soda solution in water are gradually added, the addition taking from five to ten minutes. The temperature should not be allowed to rise. When the liquid is quite transparent, it is allowed to stand for twenty minutes, and is then poured into an excess of water. The separated cinnamic aldehyde is purified by rectification. For perfumery purposes cinnamic aldehyde should be free from chlorine.

Pure cinnamic aldehyde should have a specific gravity from 1.054 to 1.057; optical rotation,  $0^{\circ}$ ; refractive index, 1.6195; and boiling point,  $253^{\circ}$ .

It is employed to a considerable extent where a powerful cinnamon odour is required without the delicacy of the natural product. It is also used in the preparation of an artificial oil of cinnamon. (*Vide* "Cinnamon.")

**CINNAMOMUM CECIODAPHNE.**—See “Nepal Sassafras.”

**CINNAMOMUM GLANDULIFERUM.**—See “Nepal Sassafras.”

**CINNAMON.**—The odour of cinnamon has from time immemorial been highly appreciated by the perfumer. The principal products of odour value are: the essential oil distilled from the bark, which is the cinnamon oil, properly so called, of commerce; and the essential oil distilled from the leaves, valued as a source of eugenol. A good deal of the oil of cinnamon distilled in Ceylon is, in fact, a mixture of bark and leaf oil.

The plant yielding these products is *Cinnamomum zeylanicum*, a native of Ceylon, found in moist low country up to an elevation of about 2,000 feet. The tree is also grown in India, Mauritius, the Seychelles, and Jamaica, but the greater part of the world's supply is derived from Ceylon. It has been stated to occur wild in the Malay Peninsula, but according to H. N. Ridley, the Director of the Botanic Gardens, Straits Settlements, this is doubtful. He has found the allied tree *Cinnamomum inero* there, and whilst it is almost impossible to detect any botanical differences between this tree and the Ceylon cinnamon, the taste and odour of the barks are quite different. He considers it probable that the true Ceylon cinnamon is a very aromatic form of *C. inero*. It is probable that the cinnamon mentioned in early writings was in fact cassia, which was certainly imported into Arabia from China in very early days.

In the sixteenth century Ceylon cinnamon was entirely derived from wild trees, and the collection of the bark was controlled by the Portuguese, who had occupied the island in 1536. About 100 years later the Dutch took the island, and in 1770 De Koke commenced the cultivation of the tree, and the Dutch obtained about 200 tons of bark annually, burning the bark when supplies were excessive in order to keep the price up.

The “cinnamon gardens” of Ceylon are situated principally in the south-west of the island. The bark is exported either in the form of pipes or quills, or in the form of chips or small fragments, the latter being used for the distillation of the essential oil. The oil distilled in Ceylon is usually obtained by macerating the chips in brine for a few days and then subjecting them to distillation. The yield varies from 0·5 to 1 per cent. A considerable amount of the bark is distilled with the addition of

leaves, or cinnamon leaf oil is added to the oil distilled from the bark. In purchasing Ceylon distilled oil it is necessary to examine the product from this point of view, as the leaf oil has none of the characteristic cinnamon odour, but closely resembles clove oil.

The oil of cinnamon bark owes its odour to its principal constituent, cinnamic aldehyde (*q.v.*), but, of course, modified by the presence of secondary constituents. The characters of the oil depend on the condition of the raw material, and also on the method of distillation employed. The oil distilled on the Continent generally possesses a higher specific gravity than that distilled in England, and that distilled in the Seychelles differs very considerably from all other bark oils. The following figures are given by E. J. Parry ("Chemistry of Essential Oils," 4th ed., vol. i.) :—

	English distilled.	Continental distilled.	Seychelles oils.
Specific gravity . . .	0.995-1.040	1.020-1.040	0.943-0.975
Optical rotation . . .	0° to — 1°	0° to — 1°	— 1° to — 3°
Refractive index . . .	1.5700-1.5850	1.5850-1.5910	1.5280-1.5335
Cinnamic aldehyde . .	58-70 per cent.	63-76 per cent.	25-36 per cent.

Ceylon cinnamon bark oil contains, in addition to cinnamic aldehyde, the following bodies: methyl-amyl ketone, pinene, phellandrene, cymene, benzaldehyde, nonylic aldehyde, cumic aldehyde, linalol, linalyl isobutyrate, eugenol, and caryophyllene.

Cinnamon leaf oil is entirely different from the bark oil. It consists mainly of eugenol (up to 95 per cent.), which can be extracted and used for the manufacture of vanillin. This oil has a specific gravity from 1.040 to 1.065; optical rotation, — 0° 10' to + 2° 35'; refractive index, 1.5300 to 1.5450; and eugenol value, 70 to 95 per cent.

It has been stated that Madagascar cinnamon leaf oil contains a considerable amount of benzyl benzoate. This requires confirmation, but the eugenol in this oil should be determined in the cold, as otherwise benzyl benzoate is decomposed and interferes with the accuracy of the determination.

Samples of cinnamon bark oil from the Gold Coast have been examined at the Imperial Institute. Three samples were reported upon in the *Bull. Imp. Inst.*, 1919, 17, 189, and compared with a sample previously reported upon (*ibid.*, 1918, 16, 146).

The three samples were as follows :—

No. 1. *From Assuantsi*.—This consisted of pieces of rolled bark, of pale reddish brown colour, about 10 inches in length and 1 inch in width. The rolls were very irregular in shape, and much scarred and torn.

The aroma of this material was inferior to that of Ceylon cinnamon bark.

No. 2. *From Coomassie*.—This sample consisted of rolls of bark measuring 12 inches in length and 1 to 1½ inches in width. The material resembled sample No. 1, but possessed a better aroma.

No. 3. *From Aburi*.—This bark was in rolls about 9½ inches long and ¾ inch wide. It was similar in appearance to sample No. 1, though somewhat paler, whilst the aroma was more fragrant than that of sample No. 1, but not equal to that of sample No. 2.

Distillation trials were carried out with the three barks at the Imperial Institute in order to determine the yields of volatile oil which they furnished, and the results are shown below in comparison with the corresponding figures for the previous sample from Tarquah referred to above :—

	Sample No. 1 from Assuantsi.	Sample No. 2 from Coomassie.	Sample No. 3 from Aburi.	Sample No. 4 from Tarquah.
	Per cent.	Per cent.	Per cent.	Per cent.
"Heavy" oil which separated from the aqueous distillate . . . . .	1·5	1·6	1·4	1·18
"Light" oil extracted with ether from the aqueous distillate . . . . .	0·3	0·4	0·3	0·30
Total yield of oil . . . . .	1·8	2·0	1·7	1·48

It will be seen that the yields of oil from the later samples are somewhat higher than that furnished by the original sample from Tarquah. They are also considerably in excess of those yielded by Ceylon cinnamon bark, which vary from 0·5 to 1 per cent.

The samples had the following characters :—

	1.	2.	3.	4.
Specific gravity . . . . .	1·038	1·042	1·041	1·042
Refractive index . . . . .	1·5940	1·6050	1·6030	1·6030
Aldehydes . . . . .	74 per cent.	88 per cent.	86 per cent.	86 per cent.

## P E R F U M E R Y

*Roure-Bertrand Fils* (*Bulletin*, October, 1920, 36) have examined a cinnamon oil from Annam, which had the following characters:—

Specific gravity . . . . .	1.051
Refractive index at 17° . . . . .	1.6090
Optical rotation . . . . .	— 0° 8'
Acid value . . . . .	2.8
Aldehydes . . . . .	95 per cent.

The root bark yields an essential oil, but it is not an article of commerce.

A Japanese plant, *Cinnamomum Loureirii*, yields an essential oil which contains about 25 to 30 per cent. of cinnamic aldehyde.

*Cinnamomum glanduliferum* (or *C. Cecidophne*?), the Nepal sassafras tree, is highly odorous, and its leaves yield an essential oil, which, however, contains little, if any, cinnamic aldehyde.

Culilavan oil is the product of the bark of *Cinnamomum Culelawan*. It contains about 60 per cent. of eugenol and somewhat resembles ordinary cinnamon leaf oil.

The so-called Brisbane "white sassafras" is *Cinnamomum Oliveri*. Its bark yields an essential oil containing phenols, but no cinnamic aldehyde.

The exports of cinnamon bark (apart from oil) from Ceylon amount to between 2,000,000 and 3,000,000 lb. per annum.

For details of the cultivation of cinnamon, its diseases, and the preparation of the bark for export, see "Spices," by H. N. Ridley (Macmillan & Co., Ltd., London).

**CINNAMEINE.**—This name is used loosely to signify the mixture of benzyl benzoate and cinnamate present in balsam of Peru, etc. Strictly, it is synonymous with benzyl cinnamate (*q.v.*).

**CINNAMYL ACETATE.**—This ester has a sweet floral odour. It has a specific gravity 1.0484, refractive index 1.5295, and boils at 262°.

**CINNAMYL BUTYRATE.**—This ester, of the formula  $C_6H_5.CH : CH.CH_2.CO_2(C_3H_7)$ , has a fine fruity odour. It must be used in very small quantities. It is prepared by the esterification of cinnamic alcohol and butyric acid. It has a specific gravity 1.023, and refractive index 1.5255.

**CINNAMYL CINNAMATE.**—This ester, known also as styracin, occurs naturally in storax and other balsamic substances, and probably, in traces, in essential oil of hyacinth. It is also prepared artificially by the esterification of the alcohol and the acid. It forms a crystalline mass melting at 44°. It has a sweet



heavy odour resembling that of balsam of Peru. Its formula is  $C_6H_5.CH : CH.CH_2.CO_2.CH : CH.C_6H_5$ . Its specific gravity is 1.040 at 25°.

**CINNAMYL PROPIONATE.**—The odour of this ester,  $C_6H_5.CH : CH.CH_2.CO_2(C_2H_5)$ , resembles that of grapes; it is used in the manufacture of fruit and floral odours.

**CISTUS CRETICUS.**—See “Labdanum.”

**CITRAL.**—Citral, or geranaldehyde,  $C_{10}H_{16}O$ , is an aldehyde, or, more properly, a mixture of two isomeric aldehydes, and is the characteristic odour bearer of lemon oil, lemongrass oil, true verbena oil, and the oil of *Backhousia citriodora*, in each case modified by the presence of subsidiary constituents. Citral as a commercial article is practically entirely extracted from lemongrass oil, as, on account of price, the oil of *Backhousia* is unable to compete. It occurs in numerous essential oils, and may be obtained by the oxidation of geraniol, nerol, and linalol. Commercially it is extracted from lemongrass oil, previously fractionated, in the form of its bisulphite compound, from which, after pressing and draining, it is removed by decomposition with a dilute acid and distillation with steam. Thus, prepared commercial citral is a pale yellow oil with an intense lemongrass odour—so powerful that, after smelling it, the nose is frequently paralysed and unable to smell anything else for some hours. It is a mixture of  $\alpha$ -citral or geranial and  $\beta$ -citral or neral. The commercial mixture and the two isomers have the following characters:—

	“Citral.”	$\alpha$ -Citral.	$\beta$ -Citral.
Specific gravity at 20° .	0.890–0.893	0.890	0.889
Refractive index .	1.488–1.490	1.4891	1.4890
Boiling point at 20 mm. .	119°	119°	118°

The principal importance of citral to the perfumer is the fact that it is the sole raw material from which ionone and similar artificial violet perfume materials can be manufactured. As such, citral is only used to a small extent in perfumes, but in certain cases it imparts a sharp odour to floral bouquets which is much appreciated. (For the conversion of citral into ionone, *vide* “Ionone.” For the determination of citral, see “Aldehydes, Determination of,” and “Lemon, Oil of.”)

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**CITRAPTENE.**—This substance is the main constituent of the non-volatile residue of lemon oil. Its formula is  $C_{11}H_{10}O_4$ , and its melting point  $146^{\circ}$  to  $147^{\circ}$ . It is a dimethoxy-coumarin.

**CITRON OIL.**—See "Cedrat Oil."

**CITRONELLA OILS.**—There are two main types of these oils, namely, "Ceylon" and "Java." Oil of the former type is produced chiefly in Ceylon, while oil of the latter type is produced in Java, Federated Malay States, and Burma.

The Ceylon type is distilled from the grass *Cymbopogon Nardus*, Rendle (Lenabatu grass) (*Bull. Imp. Inst.*, 9, 1911, 240, 333), while the Java type is distilled from the grass *Cymbopogon Winterianus* (Maha Pengiri grass) (*Kew Bulletin*, 1906, 8, 297). Both types of oil are chiefly used for perfumery purposes, and mainly in the soap industry.

**Ceylon Citronella Oil.**—This type is almost entirely distilled from grass cultivated in south Ceylon, although small quantities are also produced in the Seychelles and the island of Mayotte.

The exports of this oil from Ceylon for the year 1922 were 1,325,355 lb., and for 1923 they amounted to 1,118,619 lb. Of these the United Kingdom took 313,403 lb. in 1922, and 379,200 lb. in 1923; while the United States took 779,951 lb. in 1922, and 571,841 lb. in 1923 (*Schimmel's Bericht*, 1924, p. 14).

The oil is distilled by natives in quite primitive stills, which produce about 25 lb. of oil per day, the yield of oil being 0.5 to 1 per cent. of the grass.

Practically all the Ceylon citronella oil that is dealt in commercially is adulterated with a small quantity of kerosene, although a pure grade is obtainable under the description of "estate oil."

In order to restrict the amount of adulteration, a test was devised by Messrs. Schimmel, and this test has long been known as "Schimmel's test," and is sometimes incorporated in commercial contracts, which set out that the oil sold is "guaranteed to pass Schimmel's test."

This is purely a solubility test, and depends on the relative insolubility of kerosene in 80 per cent. alcohol. It was soon found, however, that it was not capable of detecting the presence of less than 5 per cent. of kerosene, and Messrs. Schimmel, therefore, introduced a further test, which they called the "raised test," but it has not come into general use in England or the United States.

Messrs. Schimmel's instructions (*Schimmel's Bericht*, 1923, p. 18) for carrying out these tests are as follows :—

*Schimmel's Test.*—Citronella Oil shall be soluble to a clear solution in 1 or 2 volumes of 80 per cent. alcohol (specific gravity, 0.8642 at 15° C.). This solution, on addition of further volumes of 80 per cent. alcohol, shall become not more than slightly opalescent and show no marked turbidity. The alcohol shall be added gradually, and if a turbidity does develop, further alcohol is added until the turbidity reaches a maximum. When the maximum turbidity is obtained, the solution is carefully examined to see whether any oily droplets have separated out. If no separation of oily droplets is shown, the oil is said "to pass Schimmel's test."

In no case must more than 10 volumes of alcohol be used, and the oil and alcohol mixture should not be violently shaken, as otherwise the oily droplets may become too finely divided.

In England (*P. & E. O. R.*, June, 1923, p. 179, vol. xiv., No. 6) this test is often carried out in a slightly different manner; instead of the 80 per cent. alcohol being added gradually, 10 volumes of 80 per cent. alcohol are added to 1 volume of Ceylon citronella oil; this mixture is shaken and allowed to stand for twenty-four hours, after which time no oily droplets should have separated.

*Schimmel's Raised Test.*—To the original oil 5 per cent. by volume of petroleum is added, and this mixture is then tested by the ordinary Schimmel's test.

Both these tests are purely empirical, and, while easy and convenient to carry out, are by no means conclusive proof as to the purity of the oil or the extent of the adulteration.

In 1923 large quantities of citronella oil were shipped to America and England which "passed Schimmel's test," but these oils were even more heavily adulterated with kerosene than usual; in order, however, to cover the adulteration, alcohol had been added to the oils so that they should pass Schimmel's test, and in some cases the amount of alcohol that had been added amounted to 20 per cent.

When these oils were washed with three times their volume of 1 per cent. sulphuric acid, which removed the alcohol, the washed oils no longer passed Schimmel's test, and both the specific gravity and refractive index of the washed oils were materially higher than those of the unwashed oils.

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A pure Ceylon citronella oil known commercially as "estate citronella oil" has the following characters:—

Specific gravity at 15.5° C.	0.900–0.920
Optical rotation	— 7° to — 18° (usually about — 12°).
Refractive index at 20° C.	1.480–1.490.
Acetylisable contents (as geraniol)	60 per cent.—63 per cent.
Solubility in 80 per cent. alcohol	1 in 1½ volume, and passes both Schimmel's Test and Schimmel's Raised Test.

On distillation, no fraction should distil below 160° C. (absence of alcohol and light petroleum).

The first 10 per cent. distilled under reduced pressure (20 to 40 mm.) must have a specific gravity not below 0.858, and a refractive index at 20° C. not below 1.457 (Parry's "Chemistry of Essential Oils," 4th ed., vol. i., p. 66).

When washed with three times its volume of 1 per cent. sulphuric acid, the refractive index of the washed oil should not show an increase of more than 0.0005 at 20° C. (absence of alcohol).

The characters of the usual commercial quality of Ceylon citronella oil, and which oil is sold under the description "Ceylon citronella oil passing Schimmel's test," are as follows:—

Specific gravity at 15.5° C.	0.895–0.910 (usually not less than 0.900).
Optical rotation	— 7° to — 18° (usually about — 12°).
Refractive index at 20° C.	1.479–1.485 (usually not less than 1.4815).
Acetylisable contents (as geraniol)	55 per cent.—58 per cent.
Solubility in 80 per cent. alcohol.	1 in 1½ volume, and passes Schimmel's test.

When washed with three times its volume of 1 per cent. sulphuric acid, the refractive index of the washed oil should not show an increase of more than 0.0005 at 20° C.

This oil is distinguished from pure Ceylon citronella oil by—

- (1) Its lower content of acetylisable constituents.
- (2) It usually does not pass Schimmel's raised test.
- (3) The lower specific gravity and refractive index of the first 10 per cent. distilled under reduced pressure (Parry's "Chemistry of Essential Oils," 4th. ed., vol. i., pp. 65–66).

Parry and Bennett have fractionated samples of genuine Ceylon citronella oil, samples adulterated with definite amounts of

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petroleum and resin spirits, and samples of the usual market quality of Ceylon citronella oils, and find the characters of the first 10 per cent. distilled from the oil to be as follows :—

### *Pure Citronella Oils*

	Specific gravity at 15.5° C.	Rotation in 100 mm. tube.	Refractive index at 19° C.
A	0.861	— 44°	1.4680
B	0.861	— 43°	1.4732
C	0.860	— 35°	1.4692
D	0.863	— 23°	1.4655
E	0.866	— 6°	1.4590
F	0.867	— 11°	1.4571

### *Citronella Oils mixed with Adulterants*

	Specific gravity at 15.5° C.	Rotation in 100 mm. tube.	Refractive index at 19° C.
1 E + 5 per cent. resin spirit	0.855	— 7°	1.4563
2 E + 10       "       "	0.848	— 3°	1.4545
3 E + 15       "       "	0.841	— 2°	1.4525
4 E + 20       "       "	0.833	— 1°	1.4505
5 D + 5       "       "	0.854	— 17°	1.4570
6 D + 10       "       "	0.845	— 14°	1.4515
7 D + 20       "       "	0.835	— 8°	1.4490
8 C + 10 per cent. petroleum spirit . . . . .	0.848	— 24°	1.4514

### *Adulterated Citronella Oils on the Market*

	Specific gravity at 15.5° C.	Rotation in 100 mm. tube.	Refractive index at 19° C.
1	0.822	— 26° 48'	1.4492
2	0.824	— 23° 50'	1.4504
3	0.833	— 18° 20'	1.4525
4	0.820	— 22°	1.4486
5	0.844	— 17° 30'	1.4540
6	0.836	— 29°	1.4495

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## Resin and Petroleum Spirits

	Specific gravity at 15.5° C.	Rotation in 100 mm. tube.	Refractive index at 19° C.
1. Resin spirit . . . . .	0.806	+ 4°	1.4403
2. „ „ . . . . .	0.802	+ 2° 30'	1.4425
3. Petroleum spirit (turpentine substitute) . . . . .	0.798	+ 1°	1.4435
4. „ „ . . . . .	0.801	+ 1° 30'	1.4416

The lightest fraction which Parry and Bennett obtained from the adulterated oils had a specific gravity of 0.798, an optical rotation of  $-17^{\circ}$ , and commenced to distil at  $112^{\circ}$  C. In none of the fractions was any pronounced odour observed, nor any fluorescence; hence the conclusion that resin spirit is the adulterant.

The acetylisable constituents of Ceylon citronella oil consist in the main of a mixture of geraniol and citronellal, in which the geraniol predominates, although small amounts of acetylisable compounds, such as borneol, etc., have also been identified.

Regarding the proportion of geraniol to citronellal, Messrs. Schimmel (*Schimmel's Report*, April, 1923, p. 44, and April, 1914, p. 44) have examined five samples of Ceylon citronella oil, with the following results:—

Specific gravity.	Rotation.	Total acetylisable constituents.	Geraniol. Phthalic anhydride.	Citronellal.	
				Kleber's Method. Phenylhydrazine.	Dupont's method. Oxime.
		Per cent.	Per cent.	Per cent.	Per cent.
0.9012	$-11^{\circ} 22'$	54.1	30.7	11.4	7.9
0.9016	$-11^{\circ} 28'$	57.2	33.2	11.0	8.0
0.9034	$-11^{\circ} 40'$	58.6	30.0	11.6	7.8
0.9039	$-11^{\circ} 43'$	56.3	29.8	10.8	6.7
0.9033	$-11^{\circ} 31'$	57.6	30.8	11.5	7.9

From these and the values previously obtained, Messrs. Schimmel set out the following limits:—

Geraniol . . . . .	Per cent.
Citronellal (Kleber) . . . . .	29.6–34.4
or	
Citronellal (Dupont) . . . . .	7.5–11.6
	6.5–8.0

A critical examination of the chemical constituents of a pure sample of Ceylon citronella oil carried out by Messrs. Schimmel (*Schimmel's Report*, April, 1912, p. 44) resulted in the presence of the following compounds being identified: citronellal, camphene, dipentene, borneol, geraniol, methyl-heptenone, methyl-eugenol, esters of valeric acid, a terpene of very low specific gravity, a body related to linalol, thujone, nerol, *d*-citronellol in the form of acetic and butyric esters, geranyl acetate, and a high boiling laevorotatory hydrocarbon  $C_{15}H_{24}$ .

**Java Citronella Oil.**—This oil is chiefly produced in Java, although an increasing amount is now also produced in Burma and the Federated Malay States ("Malay Citronella Oil," *P. & E. O. R.*, vol. xv., No. 4, p. 120).

For the year 1921 Java exported (*Schimmel's Bericht*, 1924, p. 17) 273,140 kg., but in 1922 this rose to 434,708 kg.

Of these quantities, 13,052 kg. and 137,944 kg. were exported to England for 1921 and 1922 respectively, while to the United States the exports amounted to 100,931 kg. for 1921, and 97,960 kg. for 1922.

In Java (*Schimmel's Bericht*, 1924, p. 17) the oil is distilled from the fresh grass, the grass being cut after the first six months, and then every four months for a period of four years, after which the plants must be replaced. There are approximately 15,000 acres in cultivation, and the yield of oil is 50 to 60 lb. per acre per year, and there are thirty-five factories employed in distilling the grass.

The characters of the oil produced in Java and Malay are practically identical, but those of Burmese oil are somewhat different.

All these oils differ materially from that of the Ceylon type, not only in odour, but also in physical and chemical characters, their main difference being much higher contents of citronellal and total acetylisable contents.

These oils are sold on the basis of their acetylisable constituents, those from Java and Malay being usually bought on a basis of not less than 85 per cent. acetylisable constituents calculated as geraniol, while for the Burmese oil an acetylisable content of 90 per cent. is often stipulated.

These oils are not often adulterated, and rarely suffer the gross adulteration that is common to Ceylon citronella, although at intervals they suffer adulteration with fatty oils (*P. & E. O. R.*, July, 1923, vol. xiv., No. 7, p. 254), and Messrs. Schimmel have examined two samples adulterated with motor spirit.

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The characters of the oil produced in Java and the Federated Malay States are as follows :—

Specific gravity at 15.5° C.	0.885–0.895
Optical rotation	0° to –3° (rarely slightly +).
Refractive index at 20° C.	1.465–1.472 (seldom less than 1.468).
Acetylisable contents (as geraniol)	80 per cent. to 92 per cent. (usually not less than 85 per cent.)
Non-volatile residue at 100° C. <sup>1</sup>	1.5 per cent. to 5 per cent.
Solubility in 80 per cent. alcohol <sup>1</sup>	1 in 2 volumes, and becoming not more than slightly opalescent in 10 volumes.

When washed with three times its volume of 1 per cent. sulphuric acid, the refractive index of the washed oil should not show an increase of more than 0.0005 at 20° C. (absence of alcohol), and as a rule the refractive index of the washed oil is slightly lower (up to 0.001) than that of the original oil.

Not more than 2½ per cent. should distil below 208° C.

The acetylisable constituents of Java citronella oil consist, in the main, of a mixture of geraniol and citronellal, in which the citronellal predominates.

Messrs. Schimmel (*Schimmel's Report*, April, 1913, p. 44, and April, 1914, p. 44) have examined seven samples with special reference to their geraniol and citronellal contents, and give the following figures :—

Specific gravity.	Rotation.	Total acetylisable contents.	Geraniol.	Citronellal.	
				Kleber's method.	Dugont's method.
		Per cent.	Per cent.	Per cent.	Per cent.
0.8913	— 2° 15'	85.4	35.3	36.0	36.6
0.8859	— 1° 45'	87.6	35.3	40.0	45.2
0.8866	— 1° 35'	88.7	36.4	40.0	46.3
0.8868	— 1° 22'	88.0	33.5	38.8	39.5
0.8883	— 1° 28'	87.5	40.1	38.7	35.4
0.8925	— 2° 11'	84.7	35.9	38.0	37.2
0.8881	— 1° 11'	91.0	37.0	36.8	40.1

<sup>1</sup> *P. & E. O. R.*, July, 1923, p. 254, vol. xiv., No. 7.



From these and previous results they suggest the following limits :—

	Per cent.
Geraniol . . . . .	26.6 40.1
Citronellal (Kleber) . . . . .	35-41
or	
Citronellal (Dupont) . . . . .	35-46

Oils produced in Burma usually have the following characters :—

Specific gravity at 15.5° C. . . . .	0.890-0.900.
Optical rotation . . . . .	0 to + 2° (very rarely slightly —).
Refractive index at 20° C. . . . .	1.469-1.472.
Acetylisable contents (as geraniol)	89 per cent. to 93 per cent.
Non-volatile residue at 100° C. <sup>1</sup> . . . . .	2 per cent. to 5 per cent.
Solubility in 80 per cent. alcohol <sup>1</sup> . . . . .	1 in 2 volumes, becoming not more than opalescent in 10 vols.

As in Java citronella oil, the acetylisable constituents of Burma citronella oil consist in the main of a mixture of geraniol and citronellal, but the amount of geraniol present is usually somewhat higher than that found in Java citronella oil, and often amounts to 50 per cent. of the oil.

Burma citronella oil is, as a rule, distinguished from that produced in Java by—

(a) The optical rotation of the Burma oil is usually to the right, while that of the Java is almost invariably to the left.

(b) The refractive index and specific gravity of the Burma oil are relatively higher for the same total acetylisable contents than those of the Java oil.

In the case of Burma citronella oil a specific gravity of 0.893 would indicate an acetylisable content of about 92 per cent., while for an acetylisable content of 90 per cent. the specific gravity would be about 0.896. In Java oil a specific gravity of 0.893 is usually found, together with an acetylisable content of about 86 per cent., while for an acetylisable content of 90 per cent. the specific gravity would be about 0.888.

Further references to citronella oil :—

“ Separation and Detection of Benzine and Petroleum ” (Dodge, *Eighth International Congress of Applied Chemistry*, 1912, vol. vi., p. 86).

<sup>1</sup> *P. & E. O. R.*, July, 1923, p. 254, vol. xiv., No. 7.

"Analysis of Oil of Citronella" (*P. & E. O. R.*, June, 1913, vol. iv., No. 6, p. 167).

"Effect of Climate on Burma Citronella Oil" (*P. & E. O. R.*, vol. v., No. 12, p. 398).

"Some Abnormal Samples of Java Citronella Oil" (*P. & E. O. R.*, vol. v., No. 8, p. 275).

"Formosan Citronella Oil" (*P. & E. O. R.*, vol. vii., No. 9, p. 279; vol. ix., No. 13, p. 323; vol. x., No. 10, p. 246).

"Specific Gravity of Ceylon Citronella Oil at Temperatures from 15° to 35° C." (*Schimmel's Bericht*, 1923, p. 19).

"Viscosity of Java Citronella Oil" (*Schimmel's Bericht*, 1924, p. 18).

M. S.

**CITRONELLAL.**—Commercial citronellal is, according to the latest researches, like citral, a mixture of two isomeric aldehydes, of the formula  $C_{10}H_{18}O$ . Of these the isomer corresponding with citronellol is citronellal, and that corresponding with rhodinol is termed rhodinal. Citronellal is the characteristic odour bearer in Java citronella oil, and also in Ceylon citronella oil; in both oils it is mixed with geraniol, the citronellal predominating in the former, and the geraniol in the latter oil. Citronellal is extracted from citronella oil by means of its bisulphite compound in the same way as citral is prepared. The oil is fractionated and the geraniol recovered by means of its calcium chloride compound, or by other suitable means, so that practically the whole of the two constituents is recovered.

Citronellal has a penetrating odour, but is only suitable for cheap perfumery. It is, however, the raw material for the manufacture of hydroxy-citronellal (*q.v.*).

Commercial citronellal is a pale yellow or colourless oil having the following characters: boiling point, 205° to 208°; specific gravity, 0.855 to 0.858; refractive index, 1.4450 to 1.4480; optical rotation, +9° to +12°, occasionally slightly lævotatory if prepared from Java oil. Prirs (*Chem. Weekblad*, 1917, 14, 692) gives the following characters for the isomers of citronellal (assuming the usually accepted constitutions of citronellol and rhodinol are correct): Citronellal—specific gravity, 0.888 at 14°; boiling point, 203° to 204°; and melting point of semi-carbazone, 85° to 86°. Rhodinal—specific gravity, 0.8745 at 14°; boiling point, 198° to 199°; and melting point of semi-carbazone, 83° to 84°.

Pure citronellal is usually obtained by extracting the unchanged

citronellal in the manufacture of citronellol from citronella oil by means of sodium bisulphite.

**CITRONELLOL.**—Citronellol  $C_{10}H_{20}O$  is an alcohol found in rose, geranium, and other essential oils. An acute controversy has for many years raged over the question of the relationships between geraniol, citronellol and rhodinol. Rhodinol was put upon the market as a specific chemical individual differing from both geraniol and citronellol, by French chemists (Barbier and Bouveault); various German chemists insisted that it was merely a mixture of the other two already well-known alcohols. Bodies named roseol and reuniol then appeared, but the most recent work of Barbier and Locquin (*Comptes Rendus*, 157, 1114) and Harries and Comberg (*Annalen*, 1915, 410, 1) has practically settled the question, and roseol and reuniol, as well, probably, as commercial rhodinol, may be regarded as impure bodies. Commercial rhodinol, however, has been shown to contain an isomer of citronellol, for which the name rhodinol has been retained. It may be taken for granted, therefore, that both citronellol and rhodinol, as met with in commerce, are mixtures of the two isomers. The following are the characters of the commercial articles which are usually obtained from citronellal by reduction, and from geranium oil :—

	From geranium oil.	From citronellal.
Boiling point at 17 mm.	—	117°–118°
Boiling point at 764 mm.	225°–226°	—
Specific gravity	0.862	0.858
Refractive index	1.4570	1.4555
Optical rotation	– 1° 40'	+ 4°

Citronellol and rhodinol have faint but sweet rose odours, and are used in the preparation of artificial otto of rose, where it is usually associated with geraniol, phenyl-ethyl alcohol, octyl alcohol, decyl and nonyl aldehydes, traces of citral and traces of phenyl-acetic acid, and various esters of geraniol and citronellol. (See also "Rhodinol.")

The following is the usual method for the preparation of citronellol by reduction of citronellal (Lewinsohn, *P. & E. O. R.*, 1923, 360) :—

Ten kilograms of aluminium turnings freed from grease by washing in petroleum ether are treated with caustic soda solution, and when hydrogen is briskly evolved the caustic solution is run off and the metal washed with water. It is then treated for a short time with 1 per cent. solution of mercuric chloride. To

9.3 kg. of aluminium so treated 54 kg. of 80 per cent. alcohol and 18 kg. of citronellal are added, and then 0.45 kg. of mercuric chloride. Reaction commences at once, and the temperature must be kept down to 35° by vigorous stirring and, if necessary, a water jacket. The reaction mass, after sixteen hours, is diluted with water and filtered, and then distilled, traces of citronellal being removed from the citronellol by treatment with sodium bisulphite.

**CITRONELLYL ACETATE.**—This ester,  $C_{10}H_{19}O.OC.CH_3$ , is a natural constituent of geranium and rose oils, and is a useful addition to most rose or geranium perfumes. Its odour recalls that of bergamot oil. It is prepared by the acetylation of citronellol, and has the following characters: specific gravity, 0.893 to 0.900; optical rotation, + 3° to - 3°; refractive index, 1.4450 to 1.4480; and boiling point, 120° at 15 mm.

**CITRONELLYL BUTYRATE.**—This ester,  $C_{10}H_{19}O.O.C.C_3H_7$ , is prepared by the suitable esterification of the alcohol. It is a useful ester to add in traces to artificial rose perfumes. Its specific gravity is 0.894, and refractive index 1.4465.

**CITRONELLYL FORMATE.**—By acting on citronellol with concentrated formic acid, citronellyl formate  $C_{10}H_{19}O.O.CH$  results. Commercial samples rarely contain more than 90 per cent. of actual ester, as the reaction is incomplete. It is an oil of specific gravity about 0.910, and refractive index 1.4510. It has a faint rose odour with a suggestion of cucumber.

**CITRONELLYL TIGLATE.**—See "Tiglic Acid Esters."

**CITRONELLYL VALERIANATE.**—This ester has a fruity odour. Its specific gravity is 0.888; and refractive index 1.4435.

**CIVET.**—Of all the animal substances used in perfumery, civet probably has the most revolting odour, closely resembling fæces in this respect. In very dilute solution, however, this odour is not noticeable, and it is an extremely valuable fixative, much appreciated for fine perfume work. It is a glandular secretion of the civet cat. The following account of the natural history of this animal is due mainly to C. C. Treatt (*P. & E. O. R.*, 1912, 73). The civet cat tribe, the *Viveridæ*, are confined to the old world. In this tribe are included other closely allied carnivores which do not produce civet, such as the mongoose and the ichneumons. All the true civet cats possess two perineal glands, forming a deep pouch in the posterior part of the abdomen, and this pouch is divided into two sacs, each about the size of a marble, in which the civet, secreted by the surrounding glandular follicles,

is stored. The civet in the pouches is at first semi-fluid, but becomes stiffer, and darkens in colour. The function of the civet bag is not known, but it is believed to be of value as a means of defence on account of its foul odour, and also for the purpose of sexual attraction. In spite of the foul odour, hounds will leave any other scent if they once cross the trail of a civet cat. The animals producing civet are the following: *Viverra zibetta*, the Indian civet of Bengal, China and Malaya; *V. civettina*, on the Malabar coast; *V. megaspila*, the Burmese civet of Burma, Cochin China, the Malay Peninsula and Sumatra; *V. tangalunga*, the Java civet of Java, Sumatra and Borneo; and *V. malaccensis*, the rasse of India, Ceylon, Assam, China, Java and Sumatra; and *V. civetta*, the African civet cat. Almost the whole of the world's supply comes from the African civet cat. It is possible that the civet produced in other districts is used locally by the natives. Although always wild, the animal will sometimes become fairly tame in captivity, and the writer (E. J. P.) has freely handled a number of the cats, which showed no tendency to bite. When, however, the civet is being collected, the cat is quite unsafe to handle. It is placed in a long cage in which it cannot turn round, and teased and irritated, as the secretion is much greater when the cat is angered. The civet is extracted from the pouch with a spatula, when it is pale yellow and semi-liquid, but hardens and darkens on exposure to the air, becoming rather stiffer than butter. It is packed in ox horns, and protected by a leather cap tied round the horn, and exported in these horns, which usually hold about 30 oz. The bulk of it comes from Abyssinia.

Civet is very frequently adulterated, the principal adulterants being gummy and saccharine matter, banana pulp, or petroleum jelly. Civet owes its odour to a mixture of skatol, possibly indol, and a ketone termed zibethone, with some free acids, ethylamine and propylamine (Sack, *Chem. Zeit.*, 1915, 39, 538). Zibethone has the formula  $C_{17}H_{30}O$ , and melts at  $32.5^{\circ}$ , boiling at  $342^{\circ}$  at 741 mm.

A pure civet should have the following characters:—

Water . . . . .	5–10 per cent.
Mineral matter . . . . .	Not exceeding 2 per cent.
Acetone extract . . . . .	Not less than 80 per cent.
Dirt, hairs, etc. . . . .	Not more than 5 per cent.
Petroleum ether extract (after acetone) . . . . .	Not more than 5 per cent.
Alcohol extract (90 per cent.) . . . . .	55–60 per cent.

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The acetone extract should have an acid value of from 85 to 115, and the melting point should be from 42° to 46°.

The alcohol extract should have an acid value of about 135, and an ester value about 30.

The following characters for pure civet are given by Schimmel & Co. (*Bericht*, 1924, 106).

		Acid value. Ester value.	
	Per cent.		
Alcohol extract . . . . .	58	138.8	29
Ether extract (after alcohol) . . . . .	19.9	9.9	81
Chloroform extract (after ether) . . . . .	1.1	18.7	124.5
Residue . . . . .	7.5	—	—
Water . . . . .	13.5	—	—

Adulteration with petroleum jelly causes a lowering of the alcohol extract, and an increase in the ether extract, the latter, of course, having a low ester value in the presence of petroleum jelly.

The following method will detect petroleum jelly in civet. Five grams are well rubbed in a mortar with 50 c.c. of acetone, until it is completely disintegrated. The mixture is allowed to settle, and the clear liquid is poured off. The residue is well mixed with another 50 c.c. of acetone and then poured on to a filter, and the insoluble matter washed with a little more acetone. The residue is now dried at a low temperature. If the civet be free from petroleum jelly, it will be greyish-white in colour and powdery, whereas if the adulterant be present, it will be oily or pasty. In this case, the residue is well mixed with 50 c.c. of petroleum ether, the liquid filtered, and the insoluble matter washed with more petroleum ether. In the presence of petroleum jelly the filtrate will almost always be fluorescent (unless the petroleum jelly has been completely de-bloomed), and the solvent can be evaporated and the adulterant weighed. A microscopic examination should demonstrate the absence of vegetable cells and fibres, which are present if vegetable pulps have been used as adulterants.

Artificial civet is a market article, but if entirely artificial lacks much of the value of true natural civet. A mixture of natural civet, however, with synthetics, is more successful, and the best "artificial civet" is so compounded. Skatol, indol, and tetrahydro-*para*-methyl-quinoline are the most useful synthetics for the purpose.

## P E R F U M E R Y

Nivière has published an account of his examination of civet (*Bull. Soc. Chim.* (4), 1920, 27, 794), which is very illuminating in indicating the results to be expected with adulterated civets.

Nivière examined four samples of civet described as pure.

	Insoluble in Benzene (cold). Per cent.	Ash in same.
Sample No. 1 . . .	6.60 ..	Trace .
„ No. 2 . . .	6.40 ..	„
„ No. 3 . . .	7.00 ..	„
„ No. 4 . . .	18.35 ..	18.15 per cent.

The ash in sample No. 4 was talc.

After distillation of the benzene from the benzene extract in a vacuum, the soluble residues were dissolved in 96 per cent. alcohol. The amounts soluble in alcohol were as follows :—

	Per cent.	
Sample No. 1 . . .	56.70	} Calculated on the original weight of the civet.
„ No. 2 . . .	57.01	
„ No. 3 . . .	55.21	
„ No. 4 . . .	38.82	

The acid numbers of the residues left after evaporation of the alcohol *in vacuo* varied little; from 103.1 (No. 1) to 111 (No. 4); and the ester numbers varied from 15.3 (No. 1) to 25.2 (No. 4).

The author continued the examination only on sample No. 2, as this presented the greatest probability of being pure.

The benzene insoluble part melted at 58° to 59°, and in it cholestérine was identified with certainty, and the following results were obtained :—

Acid number . . . . .	8.4
Ester number . . . . .	69.7
Iodine number . . . . .	68.43
Acetyl number . . . . .	80.02

These figures bear great resemblance to those furnished by waxes.

*Examination of the Alcoholic Extract.*—The solvent was removed *in vacuo* and the residue taken up with ten times its weight of benzene. The solution at first was clear and limpid, but after a few minutes it became turbid, and a deposit appeared. The insoluble part was examined after decantation. It was made up of glucose, which was identified by its physical properties and its osazone.

The acids present in the benzene solution were removed by a

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5 per cent. solution of sodium carbonate, and constituted 0.35 per cent. of the crude civet. They are liquid at the ordinary temperature, and their odour suggests caproic and caprylic acids; the average molecular weight was 168.

After washing with water, the benzene solution was exhausted with 5 per cent. sulphuric acid, and yielded skatol and some volatile bases with an odour of ethylamine and propylamine.

After removal of the solvent, the remaining fraction, 57.2 gram was fractionally distilled *in vacuo*, and yielded, at a pressure of 5 mm :—

	Gr.
(a) 145°–180° . . . . .	3.00
(b) 180°–200° . . . . .	7.00
(c) 200°–210° . . . . .	6.00
(d) 210°–220° . . . . .	20.80
(e) 220°–230° . . . . .	9.40
(f) 230°–280° . . . . .	9.00
Residue . . . . .	9.00

Several of these fractions did not possess the characteristic odour of civet: they had the odour of a fatty body somewhat rancid. The fraction (d), which was solid, smelt like rancid stearine; its melting point was not very sharp, about 70°; its acid number, 198.4; and acetyl number, 160. It was, therefore, chiefly made up of an acid containing hydroxyl, similar to those present in wool fat. Nivière concludes that this sample was adulterated with lanoline, and probably liquid glucose.

**CLARY SAGE.**—*Salvia Sclarea*, known as clary sage, or muscatel sage, yields an essential oil the value of which cannot be over-estimated for perfumery purposes. The plant is a native of the Mediterranean littoral, and has long been used by the Italians in the preparation of vermouth, and by the Germans in giving wine a "muscatel" flavour. Gattefossé is mainly responsible for having brought its great perfume value into due prominence, and in 1909 he started its cultivation on a commercial scale in the Vaucluse district. It flourishes best in the warmer districts, such as Vaucluse, Basses-Alpes, Var, Alpes Maritimes, Gard, Hérault, and Ariège. It is commonly known as muscatel sage or *toute bonne*. It prefers a light, stony soil. It is usually cut twice a year, firstly in July, and, later, in September. The first cutting is the richer in essential oil, the second being usually dried as a herb instead of being distilled. Propagation is usually effected by means of seeds, the young plant



growing to a height of about 18 inches in the first year, and 4 to 5 feet in the second year. The crude oil (or the substances extracted by means of a volatile solvent) has such a high fixative value, combined with a useful odour, that it has become known in France as *huile ambrée*, oil of amber, or vegetable ambergris. It is an expensive oil, as the yield is quite small. In distilling the oil lavender stills may be used, but rapid distillation with high-pressure steam and highly efficient condensation are essential. When the plant is conveyed by road to the distillery, there is usually a considerable time between the gathering of the plant and its distillation, so that a certain amount of fermentation takes place, and the product is less valuable than when distillation follows the cutting immediately. If the whole of the plant be distilled, including the roots, the oil may contain resinous and

District.	Esters.	Specific gravity at 20°.	Rotation.	Refractive index.
	Per cent.			
Nîmes . . .	72·5	0·983	— 11°	—
Vaucluse . .	63·7	0·895	— 15·6°	—
Villeurbanne .	62·75	0·897	— 22·1°	1·4641
„ . . .	58·8	0·901	— 23·6°	1·4660
Lorgues . . .	42·2	0·887	— 14·6	1·4655
„ . . .	45·1	0·898	—	—
„ . . .	65	0·898	—	—
„ . . .	66·7	0·894	—	—

oxygenated bodies of powerful odour. This type of oil is useful enough for fixative purposes, but is not of the delicate odour necessary for the finest perfumery purposes. Where such an oil is required, only the flowering tops should be distilled, which are encouraged by liberal manuring. The character of the oil varies with the state of maturity of the plant, the degree to which the plant has been dried, and the time and weather when the plant is cut. For example, a pure oil may contain as little as 38 per cent., or as much as 72 per cent. of esters, calculated in the conventional manner as linalyl acetate. Fine oils, distilled only from the inflorescences, are freed from resinous matter, which is separated in the distillation and dissolved in inferior grades of oil to be used solely for fixative purposes. The fine grades of oil have an exquisite odour recalling neroli, bergamot, lavender, and ambergris. It can be used in nearly any type of fine perfume,

and is of especial value to improve eau de Cologne and lavender water. It also has the effect of improving the somewhat coarse odour of artificial musk. The table on p. 161 gives the characters of authentic samples of this oil distilled in France. The esters are calculated as linalyl acetate, but their exact actual character has not yet been fully investigated (Gattefossé, *La Parfumerie Moderne*, 1922, 59).

German distilled oils have been stated to have a specific gravity 0.910 to 0.960; optical rotation,  $-25^{\circ}$  to  $-48^{\circ}$ ; and ester value, 6.5 to 56 per cent. These figures probably represent crude oils in some cases, and adulterated samples in others. The optical rotation  $-63^{\circ}$  given by the writer (E. J. P.) in "The Chemistry of Essential Oils, etc.," 4th ed., vol. ii., p. 257, is probably incorrect and represents an adulterated sample. A hybrid named *Salvia turquestiana* has been produced by Gattefossé which yields an essential oil with a slight but pronounced musk odour.

**CLAUSENA OIL.**—The leaves of *Clausena Anisum-olens* yield, according to Brooks (*Philipp. Jour. Sc.*, 1911, 6, 344), 1.2 per cent. of essential oil having a powerful aniseed odour. The oil has a specific gravity at  $\frac{30^{\circ}}{30^{\circ}}$ , 0.963, and refractive index 1.5235 at  $30^{\circ}$ . It contains 90 to 95 per cent. of methyl-chavicol.

**CLOVER, PERFUME OF.**—See "Trèfle."

**CLOVES AND CLOVE OIL.**—The clove is the unopened flower bud of *Eugenia caryophyllata*, a beautiful evergreen tree belonging to the natural order *Myrtaceæ*. It is indigenous only to a small number of islands in the Moluccas, and is cultivated in Sumatra, Penang, Malacca, Madagascar, the Seychelles, Bourbon, Mauritius, the West Indies, Zanzibar, and Pemba. The two last named islands supply the bulk of the cloves of commerce. Cloves are mentioned in Chinese works dating back as far as 260 B.C., when court officials were required to hold cloves in their mouths when addressing the emperor. Much vagueness appears to have surrounded the origin of cloves, an Arabian geographer, Ibn Khurdadbah, at the end of the ninth century describing it as a product of Java, and Marco Polo in the thirteenth century also made the same statement. Nicolo Conti, a Venetian merchant, who lived in the earlier half of the fifteenth century, was the first to discover the real source of the spice, stating that it came from Banda. The Portuguese held control of the Spice Island until

1605, when they were expelled by the Dutch. On the founding of Penang by Captain Light in 1786 the East India Company tried to break the Dutch monopoly, and the cultivation proceeded slowly, but steadily, and Penang cloves are still amongst the most highly esteemed, but the greater part of these are consumed locally, so that a great deal does not reach the London market.

The word clove is derived from the French *clou*, a nail, from the resemblance in shape of the dried bud to a nail.

The plant is generally grown from seed, but can also be propagated by means of layers. Seeds are soaked in water for several days, and when they have commenced to germinate they are planted out about 6 inches apart in shaded beds, with the bud end above the ground. The plants are kept in these beds, well shaded and watered for nearly a year. When they are about 6 inches tall the shading is removed, and they are hardened off by exposure to the sun for a month or two, and then planted out. The most suitable soil is a dark loam with a substratum of dark yellow earth mixed with gravel. In Zanzibar a red clay soil is preferred. The tree only grows successfully fairly near the coast, and is said to require sea air. The clove tree commences to produce flower buds in the fourth or fifth year after planting, in Penang and Zanzibar. In the Moluccas, this takes six to eight years. The buds are ready for gathering in August to December, in Zanzibar, and about a month later in the Straits Settlements. In the Moluccas the harvest takes place twice a year, namely, in July and December. The buds are generally picked off by hand, and are then spread out on mats to dry in the sun. In Amboyna they are first dried on a framework over a slow wood fire, which gives them a brown colour, and then are dried off in the sun, when the colour changes to black. In Zanzibar, after the clove buds are gathered, they are dried for six or seven days, during which time they lose up to 60 per cent. of their weight. Zanzibar cloves are smaller and more shrivelled, and of poorer colour, than Penang and Amboyna cloves. The best cloves are large and plump, but little wrinkled, and of a light purplish brown with a purplish bloom on them. If gathered before they are ripe, they shrink and become shrivelled badly, whilst if insufficiently dried they are liable to go mouldy. For exhaustive details of the cultivation and history of the spice, H. N. Ridley's work "Spices" (Macmillan, London, 1912), should be consulted. The flower stalks, separated from the buds whilst they are drying, are also dried and exported, and are distilled for their essential oil, which is

present to the extent of about 6 to 7 per cent., as against 12 to 18 per cent. in the buds. These stems are known in France as *griffes de girofle*. The dried fruits of the clove are known as mother cloves; these are occasionally exported, but are not usual articles of commerce.

Cloves are distilled to a very large extent, probably far in excess of any other spice. The oil is obtained to the extent of 12 to 18 per cent., sometimes even up to 21 per cent. It is used to a certain extent in medicine, to a considerable extent as a flavouring material, and on a very large scale as a raw material in the perfumery trade. A genuine clove oil has a specific gravity 1.044 to 1.070; optical rotation,  $-0^{\circ} 20'$  to  $-2^{\circ} 30'$ ; and refractive index, 1.5290 to 1.5355. It contains from 78 to 98 per cent. of eugenol.

Eugenol is the principal constituent of the oil, and upon its percentage the oil is valued. There are present also a small amount of acet-eugenol, the sesquiterpene caryophyllene, traces of eugenol ethers, vanillin, salicylic acid, methyl benzoate, amyl-methyl ketone, heptyl-methyl ketone, methyl-amyl carbinol, methyl-heptyl carbinol, benzyl alcohol, and dimethyl furfurol.

The eugenol is extracted from clove oil by absorption with a solution of caustic alkali, from which it is set free on acidification. A small quantity of eugenol is used as such in perfumery, in the manufacture of clove and carnation odours, and a certain amount is converted by heating with alkali, into its isomer isoeugenol, which has a finer carnation odour, and is used for the same perfumes. The bulk of the eugenol so obtained, however, is used for the manufacture of vanillin (*q.v.*), which is used on an enormous scale for chocolate flavouring, and to some extent also in perfumery. Eugenol is invariably determined in the oil, in practice, by means of an absorption with caustic alkali solution (*vide* "Phenols, Determination of"), but the process devised by Thoms is probably a little more accurate. (See E. J. Parry, "The Chemistry of Essential Oils," 4th ed., vol. i., p. 333.)

The oil distilled from clove stems does not differ materially from that of clove buds. A sample of the oil distilled from mother cloves was found by *Schimmel & Co.*, to have the following characters: specific gravity, 1.053; optical rotation,  $-3^{\circ} 11'$ ; refractive index, 1.5433; and eugenol value, 88 per cent. Clove leaves yield from 4 to 5 per cent. of an oil having a specific gravity 1.032 to 1.067; optical rotation,  $-0^{\circ} 30'$  to  $-2^{\circ}$ ; refractive index, 1.5320 to 1.5390; and eugenol content, 75 to 93 per cent.

The residue of clove oil from the eugenol manufacture is used as a cheap soap perfume under the name "light clove oil."

**COGNAC OIL.**—Oil of cognac is used for flavouring, and, to a small extent, in perfumery. The natural oil is obtained during the process of fermentation of the grape juice by the yeast, and is prepared by distilling the residues of the wine used for the production of brandy, or from the yeast cakes remaining after the removal of the wine. The development of the aroma of wine has been elaborately investigated by Rosenstiehl (*Comptes Rendus*, 1908, 146, 1224, 1417 ; 1908, 147, 150). He found that the particular esters developed depended, not only on the character of the grapes employed, but also on the micro-organisms that develop on the fruit. The crude oil is usually of a greenish colour, on account of traces of copper in combination with free fatty acids. If the copper be removed by shaking with tartaric acid, and the free fatty acids by shaking with dilute caustic soda solution, a purer oil is obtained. The physical characters of the oil are very variable, and to a great extent depend on the degree of rectification to which the oil has been subjected. The following values cover most genuine samples :—

Specific gravity . . . .	0.870-0.890
Refractive index . . . .	1.4270-1.4325
Optical rotation . . . .	— 0° 30' to + 0° 45'
Acid value . . . . .	25-110
Ester value . . . . .	140-250

For the occurrence of traces of methyl anthranilate in cognac oil, see Power and Kleber, *Jour. Agric. Research*, 1923, 23, 47.

It was first considered (Pelouze and Leibig, *Annalen*, 1836, 19, 241) that the chief constituent of oil of cognac was the ethyl ester of cœnanthyllic acid, and that the latter was identical with pelargonic acid obtained from rose-geranium oil. Later investigations, however, showed that oil of cognac is a mixture of esters of ethyl and amyl alcohols and capric and caprylic acids (Fischer, *Annalen*, 1861, 118, 307 ; Grimm, *ibid.*, 1871, 157, 264 ; Halenke and Kurtz, *ibid.*, 1871, 157, 270).

The term "cœnanthlic ether" is usually applied to the natural product, but artificial esters are prepared which have an odour resembling the true oil of cognac. These are the ethyl esters of cœnanthyllic and pelargonic acids.

Cœnanthyllic acid  $\text{CH}_3(\text{CH}_2)_5\text{COOH}$  is normal heptic acid, and is obtained by the oxidation of cœnanthol, produced by the

destructive distillation of castor oil. It is also formed by the oxidation of normal heptyl alcohol and of oleic acid, and by the reduction of dextrose-carboxylic acid. It is an oily liquid boiling at 220° to 223°, and has a specific gravity of 0.918 at 20°.

Cenanthal, cenanthic aldehyde or normal heptylic aldehyde is obtained by the dry distillation of alkaline ricinoleate. Castor oil, which consists essentially of the glycerides of ricinoleic acid, is rapidly distilled until a resinous residue remains, the greater part of the ricinoleic acid being converted into cenanthal and higher fatty acids. The distillate is rectified and the portion distilling between 90° and 180° shaken with a saturated solution of sodium bisulphite, warmed, and filtered. The salt, which separates on cooling, is pressed between filter paper, mixed with sodium carbonate, and distilled in a current of steam. The cenanthal which floats on the distillate is separated and dried over anhydrous sodium sulphate. A better yield is obtained by distilling the ethyl or methyl ester of ricinoleic acid.

Ethyl pelargonate is prepared by the action of dilute nitric acid on oil of rue. The oil is treated with twice its weight of dilute nitric acid and heated until the mixture begins to boil. Two layers are formed, the upper one containing the chief products of oxidation. The lower layer is freed from nitric acid by heating on a bath containing a solution of zinc chloride. The two liquids are then filtered, and the pelargonic acid is converted into the ethyl ester by esterification with alcohol, and purified by steam distillation.

**CONCRETES.**—See “Extraction of Perfume from Plants.”

**CONVALLARIA MAJALIS.**—This is the lily of the valley. The perfume is prepared in the form of a concrete or absolute, but as found in the market is mainly synthetic. (See “Lily” and “Muguet.”)

**CONVOLVULUS OIL.**—The wood of *Convolvulus scoparius* and *C. floridus*, both indigenous to the Canary Islands, yields a small quantity of essential oil, which is the true rosewood oil, or oil of rhodium. It is a liquid which solidifies at low temperatures, melting again at 11° to 12°. Its general characters are not known with certainty, as the authenticity of most samples examined is doubtful. The oil as met with in commerce is almost entirely an artificial mixture. It is used in soap perfumery, and must not be confused with the oil of *Bois de Rose*.

**CORIANDER, OIL OF.**—This oil, occasionally used in perfumery, for example in traces in eau de Cologne, is distilled from the ripe fruits of *Coriandrum sativum*, a native of the Levant and southern Europe. The oil contains *dextro*-linalol, pinene, and other constituents not yet identified. It has a specific gravity 0.870 to 0.885; optical rotation,  $+7^{\circ}$  to  $+14^{\circ}$ ; and refractive index, 1.4635 to 1.4760. (For the history, etc., of this spice, see Ridley, "Spices," p. 384.) Indian distillates sometimes have a refractive index as low as 1.4569.

**CORIANDROL.**—An old name for impure linalol when extracted from coriander oil.

**CORYLOPSIS.**—The Japanese plant *Corylopsis spicata* bears highly odorous flowers which have a heavy, somewhat sickly odour, like that of many orchids or lilies. The perfume is not extracted, but the name is applied to fancy perfumes which have some slight resemblance to the natural odour. These are usually based on infusions of rose, jasmine, tuberose and orange flowers, with the addition of a little vetivert or patchouli oil, hydroxy-citronellal, terpeneol, ylang-ylang oil, and a trace of artificial essence of strawberry.

**COUMARIN.**—Coumarin is one of the most important of the artificially prepared perfumes. It is the substance to which the Tonquin bean (Tonka bean) owes its odour; it is found in appreciable quantity in the leaves of the American "deer's tongue," *Liatris odoratissima*, and has been found in a large number of other plants in smaller quantity (*vide* E. J. Parry, "The Chemistry of Essential Oils," 4th ed., vol. ii., p. 272). Commercial coumarin is invariably the artificial product. It was first prepared synthetically by W. H. Perkin (*Chem. Soc. Jour.*, xxi., 53, 181) by heating salicylic aldehyde (*q.v.*) with acetic anhydride and sodium acetate. Tiemann and Herzfeld heat 3 parts of salicylic aldehyde, 5 parts of acetic anhydride, and 4 parts of fused sodium acetate on an oil bath for twenty-four hours. Water is then added, and the oil which is precipitated is separated. This consists of acetyl-*ortho*-coumaric acid, with a little coumarin. This acid is decomposed by heating it to a little below its melting point ( $146^{\circ}$ ) into acetic acid and coumarin. Raschig first prepares *ortho*-cresol carbonate by the action of phosgene on *ortho*-cresol in the presence of pyridine. A current of chlorine is passed through this ether at  $180^{\circ}$ , which results in the formation of di-chlor-*o*-cresol carbonate. On hydrolysis this

yields salicylic aldehyde, from which coumarin is prepared as above described. Hugo Weil has patented a method depending on the reduction of salicylic acid by sodium amalgam in the presence of boric acid. The salicylic aldehyde is, as it is formed, combined with paratoluidine. For example, 15 parts of salicylic acid, 5.5 parts of sodium carbonate, 1,000 parts of water, 18 parts of toluidine, 250 parts of salt, and 15 parts of boric acid are mixed and treated with 325 to 425 grams of a 2 per cent. sodium amalgam. The liquid is kept acid by the addition of boric acid. The *ortho*-oxy-benzylidene-paratoluidine is filtered off and dissolved in a faintly acid solution which, on steam distillation, yields salicylic aldehyde, which is converted into coumarin in the usual manner.

Coumarin is a highly odorous substance melting at  $68^{\circ}$ , and having the characteristic odour of Tonquin beans. It is a basic material for all perfumes of the type of *foin-coupé*, or "new-mown hay."

It is often adulterated with acetanilide and with terpin hydrate. The former is detected by heating the sample with a solution of caustic potash and adding a few drops of chloroform, when, on boiling, the intense odour of phenyl isocyanide is evolved. Terpin hydrate is recognised by boiling the crystals with dilute sulphuric acid, when the odour of terpineol is at once noticed.

**CRATEGINE.**—This body is identical with anisic aldehyde, either pure or in a reduced condition.

**CRATEGUS OXYCANTHA.**—See "Hawthorn."

**CREOSOL.**—This body is a diphenol,  $C_7H_6(OH)_2$ , occurring in oil of ylang-ylang. It is an odorous oil, boiling at  $220^{\circ}$ .

**CRESOL (META-).**—This body is a crystalline substance of the formula  $C_7H_8O$ , melting at  $4^{\circ}$ , and boiling at  $201^{\circ}$ . It occurs to a small extent in essential oil of myrrh. It is used in the manufacture of artificial musks. It is a colourless liquid of specific gravity 1.0375, crystallising at  $10^{\circ}$  to  $12^{\circ}$ , and boiling at  $202^{\circ}$  to  $203^{\circ}$ .

**CRESOL (PARA-).**—This body, isomeric with *meta*-cresol  $C_7H_8O$ , is a crystalline body melting at  $36^{\circ}$ , and boiling at  $199^{\circ}$ . It is found in the oils of jasmin and cassie flowers.

**CRESOL (PARA-) BUTYL ETHER.**—This ether,  $C_7H_7 \cdot O \cdot C_4H_9$ , is prepared by the condensation of *para*-cresol and butyl



alcohol by means of hydrochloric acid. It is useful in the preparation of artificial ylang-ylang and similar odours.

**CRESOL (PARA-) METHYL ETHER.**—This body, of the formula  $C_7H_7.O.CH_3$ , is a natural constituent of ylang-ylang and other flower oils. It is a colourless liquid, darkening on keeping, with a powerful odour, which recalls that of wallflower, on dilution. It boils at  $175^\circ$ , and yields anisic aldehyde on oxidation. It is essential for the production of artificial flower oils of the ylang-ylang and wallflower types. It is prepared artificially by condensing *para*-cresol with methyl alcohol by means of hydrochloric acid. Its specific gravity is 0.975 to 0.977, and refractive index 1.5130.

**CRESYL (META-) PHENYL ACETATE.**—This body is isomeric with the corresponding *para*-cresyl derivative. It has a sweet, heavy odour, and is useful in the preparation of ylang-ylang and other exotic floral perfumes.

**CRESYL OXIDE.**—There are three cresyl oxides, corresponding with the three isomeric cresols. They have the formula  $(C_7H_7)_2O$ . The best known is the di-*ortho*-cresyl oxide, which boils at  $275^\circ$ . It is prepared by dehydrating cresol, or by distilling cresylate of aluminium, or by condensing bromotoluene with cresylate of potassium in the presence of finely powdered copper. It is useful as a variant of phenyl oxide in the preparation of artificial geranium perfumes.

**CRESYL (PARA-) ACETATE.**—This acid ester of cresol  $CH_3.COO.C_7H_7$  is prepared by the interaction of *para*-cresol and acetic anhydride, or of the sodium compound of the phenol and acetyl chloride. It has been known as narceol. It has a powerful narcissus odour. It has a specific gravity 1.0528, and refractive index 1.5040.

**CRESYL (PARA-) PHENYL ACETATE.**—This body is of a sweeter narcissus odour than the corresponding acetate. It has the constitution  $C_6H_5.CH_2COO.C_7H_7$ .

**CROPS, TIMES OF FRENCH FLOWERING.**—The usual times at which the more important of the French flowers are gathered for treatment are as follows :—

<i>February–March</i>	.	.	Cassie, violet, mimosa, hyacinth.
<i>April</i>	.	.	Jonquil, hyacinth, narcissus, violet, carnation.

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May . . . .	Jonquil, narcissus, orange flowers, rose, rosemary, thyme, broom, carnation.
June . . . .	Rose, petitgrain, mignonette, carnation.
July . . . .	Jasmin, lavender, rose, rosemary, thyme, tuberose.
August–September . . . .	Tuberose, lavender, jasmin.
October–November . . . .	Cassie, jasmin.

**CULILAVAN OIL.**—Culilavan oil is distilled from the bark of *Cinnamomum Culiawan*. It is an oil of specific gravity 1.050 to 1.055, and contains about 60 per cent. of eugenol, with a small quantity of methyl eugenol and terpineol.

**CUMIC ALDEHYDE.**—This body (*p*-isopropyl benzaldehyde  $C_{10}H_{12}O$ ) is a natural constituent of cassie flower oil, but is found to a much larger extent in cummin oil. It has a powerful odour, and should only be used in traces in floral perfumes. It has a specific gravity 0.982, and boils at  $236^{\circ}$ .

**CUNNINGHAMIA SINENSIS.**—This tree, growing in Tonkin, yields a wood which is known as “coffin wood,” or “san-mou.” This is used to make coffins which are said to be indestructible, joss sticks, and other preparations for burning. Gardies (*La Parfumerie Moderne*, 1923, 110) has examined the essential oil, which has an odour of terpineol and cedrol, and found it to have the following characters: specific gravity, 0.957; optical rotation,  $-23^{\circ} 6'$ ; refractive index, 1.4932; esters, 7.4 per cent.; and free alcohols, 29.4 per cent.

**CUS-CUS.**—See “Vetivert Oil.”

**CYCLAMEN.**—There is no natural perfume extracted from the cyclamen as a commercial article. Various species of perfume-bearing plants are found growing wild in the Alpine regions, of which *Cyclamen persicum* is one of the sweetest scented. The odour of the flowers is of the amaryllis or lily type, and is “matched” to some extent—but only as a fancy perfume which does not, in fact, reproduce the odour of the flower—by the use of hydroxycitronellal, ionone and phenyl-acetic aldehyde, with traces of terpineol, and some weak floral basic perfume such as cinnamic alcohol. A trace of acetic ether gives tone to this perfume.

**CYCLOGERANYL ACETATE.**—This ester  $C_{10}H_{17}.COO.CH_3$  does not occur naturally. It is prepared by the action of phosphoric acid on geranyl acetate at a low temperature, and by

then dehydrating the glycol so formed by means of phosphoric acid at 40°. It is an ester with a sweet odour of fresh flowers.

**CYMBOPOGON OILS.**—See under Citronella, Lemongrass, Palmarosa, and Gingergrass Oils. Also “Cymbopogon Nervatus, Oil of,” etc., and under “Grasses (Perfumed) of India and Ceylon.”

**CYMBOPOGON CÆSIUS.**—This grass is closely allied to *C. Martini*, but is distinctly different. Where the two grasses meet, transition forms occur in which the two species unite completely. Few details as to the oil are available. (See *Administrative Report of the Government Botanic Gardens and Parks in the Nilghiris for 1901*, p. 5. See “Inichi Grass.”)

**CYMBOPOGON COLORATUS.**—Samples of the oil distilled from this grass in the Fiji Islands examined at the Imperial Institute (*Bull. Imp. Inst.*, 1912, 10, 27) were found to have the following characters: specific gravity, 0.911 to 0.920, and optical rotation,  $-7^{\circ}$  to  $-11^{\circ}$ . One sample contained 40 per cent. of aldehydes, principally citral, 23 per cent. of geraniol, and 10 per cent. of esters, principally geranyl acetate. A second sample contained 15.6 per cent. of geraniol, and from 45 to 50 per cent. of citronellal.

**CYMBOPOGON JAVANENSIS.**—This grass yields a highly aromatic essential oil with a sweet odour, resembling palmarosa oil. It has been examined by Hofman (*Pharm. Werkblad*, September 6th, 1919). It had a specific gravity 0.975; optical rotation,  $-3^{\circ}$ ; refractive index, 1.5135; acid number, 1.25; geraniol content, 48 per cent.; esters, 14.3 per cent.; and methyl-eugenol, 30 per cent. Citral, *lævo*-pinene and methyl-isoeugenol are also present in the oil.

**CYMBOPOGON NERVATUS.**—This plant is the Naal grass, found very widely distributed in the central portions of the Sudan, being abundant in the Blue Nile, Fung, and Kordofan provinces. The grass, when collected in full flower, in the autumn, yields the highest amount of oil—varying from 0.8 to 1.5 per cent. of the weight of the dried grass. The inflorescence alone is of value for distillation, as the stalks contain very little oil. The oil was reported upon by Schimmel & Co. (*Report*, April, 1911, 19), but from details published by Joseph and Whitfield (*P. & E. O. R.*, 1922, 175), it is probable that the oil they examined was not a genuine one. The oil obtained by these chemists was pale yellow in colour, and in odour closely resembles gingergrass

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oil—the so-called “Sofia oil” distilled in India from *Cymbopogon Martini*. Three samples had the following characters :

	1.	2.	3.
Specific gravity at $\frac{20^{\circ}}{20^{\circ}}$ . . . . .	0.954	0.955	0.953
Refractive index . . . . .	1.495	1.492	1.495
Optical rotation . . . . .	— $31^{\circ}$	— $35^{\circ}$	— $50^{\circ}$
Acid value . . . . .	—	3.6	4.4
Ester value . . . . .	29.6	21.8	26.5
Ester value, after acetylation . . . . .	198	189	189

Naal oil contains *lævo*-limonene and perillic alcohol.

**CYMBOPOGON POLYNEUROS.**—This grass, growing freely in Ceylon, yields an odorous essential oil having the following characters: specific gravity, 0.936 to 0.951; optical rotation,  $+ 31^{\circ}$  to  $+ 53^{\circ}$ , and containing 38 to 52 per cent. of aromatic alcohols.

**CYPERUS ROTUNDUS, OIL OF.**—Joseph and Whitfield (*vide P. & E. O. R.*, 1922, 176) have described this oil, which is known as Seid oil. The plant grows in the Nuba Mountains province, about twenty miles to the east of the White Nile, and about 350 miles south of Khartoum. The plant, which is a sedge, grows freely in the Sudan, and the rhizomes yield 0.5 per cent. of an aromatic essential oil, of specific gravity at  $\frac{20^{\circ}}{20^{\circ}}$ , 0.955; optical rotation,  $- 20^{\circ}$ ; and refractive index, 1.4967 at  $25^{\circ}$ .

**CYMBOPOGON SENNAARENSIS, OIL OF.**—The so-called mahareb grass of the British Sudan yields about 1 per cent. of a fragrant essential oil, which somewhat recalls pennyroyal. Roberts (*Jour. Chem. Soc.*, 1915, 1465) states that it has a specific gravity 0.938 to 0.942; optical rotation,  $+ 29^{\circ}$  to  $+ 34^{\circ}$ ; and ester value after acetylation, 60 to 62. The oil contains pinene and limonene, menthenone, a sesquiterpene alcohol, an alcohol of rose-like odour, higher fatty acids in the form of esters, traces of a phenol, and one or more sesquiterpenes.

**CYMYLACETIC ALDEHYDE.**—This body (1-isopropyl-4-ethanal-benzene), of the formula  $(\text{CH}_3)_2\text{CH}.\text{C}_6\text{H}_4.\text{CH}_2.\text{CHO}$ , is obtained by the condensation of magnesium cymyl chloride with

ethyl orthoformate, hydrolysing the product with dilute sulphuric acid, and separating the aldehyde by means of its bisulphite compound. It is a pale yellow liquid, boiling at 243°. It has a strong verbenal odour, and may find employment in synthetic perfumery (Best, *Comptes Rendus*, 1923, 550).

**DACRYDIUM FRANKLINII, OIL OF.**—The leaves of *Dacrydium Franklinii*, which grows only in Tasmania, where it is known as the Huon pine, yield 0.5 per cent. of essential oil having the following characters:—

Specific gravity	. . . . .	0.8677
Optical rotation	. . . . .	+ 20.5°
Refractive index	. . . . .	1.4835

It consists mainly of terpenes, but there is also present a small amount of methyl-eugenol.

The wood yields about 0.5 per cent. of oil having the following characters:—

Specific gravity at 18°	. . . . .	1.035–1.044
Optical rotation	. . . . .	+ 0.6° to + 1.4°
Refractive index at 23°	. . . . .	1.5316–1.5373
Acid value	. . . . .	0.9–3.1
Ester value	. . . . .	1.5

This oil consists almost entirely of methyl-eugenol. It has recently been examined at the Imperial Institute (*Bulletin*, vol. xxii., No. 3, 1924) and the following results recorded:—

Specific gravity at 15/15° C.	. . . . .	1.040
Optical rotation $\alpha_D$	. . . . .	— 3.75°
Refractive index $n_D$	. . . . .	1.533
Acid value	. . . . .	0.8
Ester value before acetylation	. . . . .	0.9
Ester value after acetylation	. . . . .	11.2
Solubility in 70 per cent. alcohol	. . . . .	Soluble in 1.5 vols.

On distillation, about 90 per cent. of the oil passed over between 250° and 253° under 755 mm. pressure, and consisted essentially of methyl-eugenol. The results of the investigation show that the composition of the present sample of Huon pine oil agreed with that recorded for the oil by previous observers. Methyl-eugenol is used to some extent in perfumery, but no regular demand has hitherto arisen for Huon pine oil, although it is clear from the results of the inquiries made by the Imperial Institute that there is likely to be a demand for it if it can be supplied in commercial quantities and at a reasonable price.

**DAFFODIL PERFUMES.**—These are merely variations of narcissus odours, or, in fact, often identical except in name. (*Vide* “Narcissus.”)

**DALBERGIA CUMINGIANA, OIL OF.**—According to Boorsma (*Bull. du Dép. d'Agricult. aux Indes Néerl.*, 1907, 7, 25), the wood of *Dalbergia Cumingiana*, which is found in Dutch East Indies, yields about 0.5 per cent. of an essential oil of aromatic odour having the following characters:—

Specific gravity at 26°	0.891
Optical rotation	— 4° 31'
Ester value	5
Ester value after acetylation	116

The wood is known locally as *kaju laka*.

**DARWINIA OILS.**—The essential oils of several species of *Darwinia*, growing in Australia, have been found to have distinct perfume value. They have been investigated by Baker and Smith (*Jour. & Proc. Royal Society New South Wales*, 1899, 163 and 1916, 181). The oil distilled from *Darwinia fascicularis*, a shrub found in the neighbourhood of Port Jackson, was obtained to the extent of 0.45 per cent. It has a specific gravity 0.915, is slightly dextrorotatory, and contains from 55 to 63 per cent. of geraniol, mostly in the form of geranyl acetate. The oil from *Darwinia taxifolia* has a specific gravity 0.876, and an optical rotation — 6.5°. It contains a small amount of an alcohol, which is probably linalol. The oil from *Darwinia grandiflora* (originally known as *D. taxifolia*, var. *grandiflora*) has been examined by Baker and Smith, and more recently by Penfold (*Jour. and Proc. Royal Soc. N.S.W.*, lvii., 237). The oil has a specific gravity from 0.901 to 0.9165; and optical rotation, + 18.25° to + 27.65°. The oil contains *dextro*-pinene, a sesquiterpene alcohol, and esters of an alcohol which has, provisionally, been named darwinol. This body has the formula  $C_{10}H_{18}O$ , and possesses the following characters:—

Boiling point at 10 mm.	108° to 111°
Specific gravity	0.9559
Optical rotation	+ 38.6°
Refractive index	1.4918

**DAUCUS, OIL OF.**—The seed of the common carrot (*Daucus Carota*), yields an essential oil which has a distinct perfume value. The yield is from 1 to 1.5 per cent., and the oil has the following characters: specific gravity, 0.870 to 0.945;

optical rotation,  $-11^{\circ}$  to  $-40^{\circ}$ ; refractive index, 1.4820 to 1.4920; and ester value, 17 to 55. The oil contains terpenes, and a divalent sesquiterpene alcohol,  $C_{15}H_{26}O_2$ , melting at  $115^{\circ}$  to  $116^{\circ}$ , and which has been named daucol. *Roure-Bertrand Fils (Bulletin, April, 1912, 30)* have examined the oil distilled from the entire plant at the period of maturity of the seed, and found it to have a specific gravity 0.902; optical rotation,  $-7^{\circ}$ ; and saponification, 195. The essential oil of the closely allied *Daucus Gingidium* has a rather finer odour than the ordinary carrot oil. It is practically identical in general characters with carrot oil, containing daucol as its odorous constituent. The oil has an odour recalling that of orris oil, and is of great value in toning down the somewhat crude odour of pure ionone and similar synthetic violet oils.

**DECALEPIS HAMILTONII.**—By the steam distillation of the crushed fresh roots of *Decalepis Hamiltonii*, a plant used chiefly as a condiment in Mysore, a brownish solid substance has been obtained which crystallises in the condenser. Treated with a little animal charcoal and redistilled, it forms a pure white crystalline body melting sharply at  $41^{\circ}$ . It is probably identical with the crystalline body isolated by Goulding and Pelly (*Proc. Chem. Soc.*, 1908, 62, 1911, 235) from a species of chlorocodon roots. It has an aromatic odour similar to that of vanillin.

**DECINE CARBONATES.**—See “Heptene Carbonates.”

**DECYL ALCOHOL.**—This alcohol,  $CH_3(CH_2)_8CH_2OH$ , is the most useful of the higher fatty alcohols (*vide* “Alcohols, Higher Fatty”). It melts at  $-10^{\circ}$ , and boils at  $231^{\circ}$ . It is exceedingly useful for giving a new tone to floral odours. Its specific gravity is 0.833.

**DECYL ALDEHYDE.**—See “Aldehydes, Higher Fatty.”

**DEMENTHOLISED PEPPERMINT OIL.**—See “Peppermint Oil.”

**DEODAR.**—See under “Cedarwood Oil.”

**DEPILATORIES.**—These substances rank among the less dignified articles included in the perfumer's art. Comparatively large quantities are exported to the East, and many women in the West elect to risk damage of a disfiguring nature to their skins for the sake of removing superfluous hairs. Alkaline sulphides are the basis of many of these preparations, calcium hydrosulphide, strontium hydrosulphide, sodium sulphide and barium sulphide being those principally used, frequently in admixture with

powdered quicklime, and diluted with starch, sugar or talc. These preparations convert the hairs into a gelatinous mass, but only attack *normal* skins after repeated employment. Rushma, a favourite preparation in the Eastern harems (*vide* Durvelle, "Perfumes and Cosmetics," p. 313) is essentially a preparation of arsenic sulphide (orpiment) and lime with a little sulphur. Thallium acetate, in combination with zinc oxide, has been recommended as a depilatory; it appears to be very powerful, but not to attack the roots of the hair, so that its effect is quite temporary.

**DEVARDARI OIL.**—The wood of *Erythroxylon monogynum*, the so-called bastard sandalwood of India, yields about 0.25 per cent. of an odorous essential oil having the following characters: specific gravity, 0.983; optical rotation,  $+16^\circ$ ; refractive index, 1.5140; and containing about 40 per cent. of a sesquiterpene alcohol. The oil has a sandalwood odour, and is of use in cheap perfumery where this odour is required.

**DHELM WANGI.**—This plant, also known as *Tilam wangi* or *Dilem wangi*, is the true patchouli, under cultivation, as a rule, for distillation purposes. *Dhelum outan* is a wild patchouli, of unknown botanical origin, which is sometimes added to the true leaves for distillation. (*Vide* "Patchouli Oil.")

**DIACETINE.**—This is an artificial ester, or a constituent of commercial triacetine, which is used for adulterating ester-containing oils. It is a practically odourless body, having a specific gravity 1.184, and boiling point  $260^\circ$  to  $265^\circ$ . One part of this body indicates 2.22 parts of esters returned as linalyl acetate. (*Vide* "Esters, Artificial.")

**DIACETYL.**—This body is a diketone,  $\text{CH}_3\text{CO.CO.CH}_3$ , found in the distillation waters of sandalwood, orris, savin, caraway, and various other essential oils. It has a specific gravity 0.9734, and boils at  $87^\circ$  to  $88^\circ$ .

**DIANTHUS PERFUMES.**—See "Carnation."

**DICITRONELLOXIDE.**—Java critonella contains a compound,  $\text{C}_{20}\text{H}_{34}\text{O}$ , which Spornitz (*Berichte*, 47, 2478) has named dicitronelloxide. It boils at  $182^\circ$  to  $183^\circ$  at 12 mm., has a specific gravity, 0.920 at  $20^\circ$ ; optical rotation,  $-4^\circ$ ; and refractive index, 1.4918.

**DICTAME BLANC, OIL OF.**—The oil known as *essence de dictame blanc ou calament*, which was distilled in Oran, Algiers,



has been examined by *Schimmel & Co.* (*Report*, October, 1906, 84). It is in all probability derived from *Amaracus dictamnus*, one of the *Labiatae*. The oil is of a pale straw yellow colour, with a strong odour of pulegone, which is present to the extent of about 85 per cent. The oil has the following characters:—

Specific gravity	. . . . .	0.935
Optical rotation	. . . . .	+ 6°
Acid value	. . . . .	2.3
Ester value	. . . . .	20.9
Ester value after acetylation	. . . . .	80

It probably contains borneol and menthol.

**DICYPELLIUM CARYOPHYLLATUM, OIL OF.**—The bark of *Dicypellium caryophyllatum*, one of the *Lauraceae*, found in Brazil, yields about 4 per cent. of a pale yellow oil having a powerful odour of cloves and containing much eugenol.

**DIETHYL SUCCINATE.**—See “Ethyl Succinate.”

**DIHYDROCARVEOL.**—Dihydrocarveol,  $C_{10}H_{18}O$ , is a natural constituent of caraway oil, and may be prepared by the reduction of carvone. It is an oil of agreeable odour, which, when prepared in as pure a state as possible from caraway oil, has a specific gravity, 0.937; optical rotation,  $-6^{\circ} 14'$ ; refractive index, 1.4836; and boiling point,  $225^{\circ}$ . Prepared artificially by treating 20 grams of carvone in 200 c.c. of absolute alcohol with 24 grams of sodium, it has a specific gravity 0.927 at  $20^{\circ}$ , and refractive index 1.4817. It exists in both optically active varieties, according to the optical activity of the carvone from which it is prepared.

**DIHYDROCARVEOL ACETATE.**—This ester has been identified in American oil of spearmint.

**DIHYDROCARVONE.**—This ketonic compound, of the formula  $C_{10}H_{16}O$ , is found to a small extent as a natural constituent of caraway oil, and is prepared artificially by the oxidation of dihydrocarveol by means of chromic acid in acetic acid solution. It is an oil having an odour recalling that of menthone and carvone, and has the following characters: specific gravity, 0.930; boiling point,  $222^{\circ}$ ; refractive index, 1.4711; and optical rotation,  $-16^{\circ}$ .

**DIHYDROCUMINIC ALCOHOL.**—*Schimmel & Co.* (*Bericht*, April, 1904, 53 and October, 1904, 41) isolated an alcohol from

gingergrass oil which boiled at  $226^{\circ}$  to  $227^{\circ}$ , and had a specific gravity, 0.951; optical rotation,  $-13^{\circ} 18'$ ; and refractive index, 1.4963. They termed this dihydrocuminic alcohol. It had an odour recalling that of a mixture of linalol and terpineol. It has now, however, been shown by Semmler and Zaar (*Berichte*, 44, 460) to be identical with perillic alcohol (*q.v.*). Elze (*Chem. Zeit.*, 1910, 34, 1175) has claimed more recently to have isolated 15 per cent. of the true dihydrocuminic alcohol from German oil of spearmint. This had a specific gravity 0.9539; and optical rotation,  $-30^{\circ} 15'$ . It yielded a naphthyl-urethane melting at  $146^{\circ}$  to  $147^{\circ}$ , and when oxidised yields an aldehyde, dihydrocuminic aldehyde, which forms a semicarbazone melting at  $198^{\circ}$  to  $199^{\circ}$ . These figures are so close to those of the corresponding ones for perillic alcohol as to make it probable that Elze's body is also identical with the last named, and is not dihydrocuminic alcohol.

**DIHYDROCUMINIC ALDEHYDE.**—The essential oil of the wood of *Hernandia peltata* contains, according to Schimmel & Co. (*Bericht*, April, 1915, 54), this aldehyde,  $C_{10}H_{14}O$ . The same body is present in the oil from the leaves of *Perilla arguta*, a Japanese oil known as Shiso, and is now known as perillic aldehyde, and as its constitution is apparently decided, and is not that of dihydrocuminic aldehyde, it is probable that the latter does not actually exist in the essential oils mentioned.

**DIHYDROFARNESOL.**—Verley (*Bull. Soc. Chim.* 1924, 35, 606) claims to have synthesised a new sesquiterpene alcohol, which he names dihydrofarnesol. It is an amber-coloured oil having an odour resembling cedarwood. Its constitution is  $CH_2 : C(CH_3)(CH_2)_3.C(CH_3) : CH(CH_2)_2CH(CH_3)CH_2.CH_2OH$ .

Farnesol is oxidised to farnesal, and this is converted into a glycidic ester, which on reduction yields dihydrofarnesol.

**DIHYDROIONONE.**—The isomeric ionones yield two different dihydroionones on reduction. These bodies are of no practical importance in perfumery, but are of great value in establishing the identity of the isomeric ionones (*q.v.*).

**DIHYDROXYTHYMOQUINONE.**—This body has been found in the essential oil of *Monarda fistulosa* by Miller (*Circular* 4, 1918, University of Wisconsin).

**DILEM OIL.**—A name given to Java patchouli oil. (See "Dhelum" and "Patchouli.")

**DILL-APIOL.**—This body is a constituent of East Indian, Spanish, and Japanese dill oils. It is isomeric with ordinary parsley apiol,  $C_{12}H_{14}O_4$ , differing from it only by the relative positions of the side chains. It boils at  $285^\circ$ ; has a specific gravity, 1.164 at  $\frac{13^\circ}{4^\circ}$ ; and refractive index, 1.5278 at  $25^\circ$ . *Iso*-dill-apiol, a second isomer of ordinary apiol, is found in the essential oil of *Piper acutifolium*.

**DILL, OIL OF.**—The essential oil distilled from the seed of *Anethum graveolens* is known as oil of dill. The plant is indigenous to central and southern Europe, but is found in many other localities. A plant growing largely in India has been described as *Anethum sowa*, but the botanical difference between the plants is not yet settled. The odour of dill oil is similar to that of caraway oil, with, however, a distinct difference. It is a mixture of limonene and carvone, with traces of other bodies, but the carvone is present in less amount than in caraway oil. European dill oil has the following characters:—

Specific gravity	. . .	0.895 to 0.918
Optical rotation	. . .	+ $70^\circ$ to + $83^\circ$
Refractive index	. . .	1.4830 to 1.4900
Carvone	. . .	30 to 60 per cent.

Indian dill oil always has a much higher specific gravity, this figure usually varying between 0.945 and 0.970. Its optical rotation is +  $40^\circ$  to +  $50^\circ$ . This oil contains a body,  $C_{12}H_{14}O_4$ , isomeric with ordinary apiol from parsley oil, and which has been named dill-apiol. J. C. Umney (*P. & E. O. R.*, 1910, 290) has examined an African dill oil which was distilled from plants grown from English seeds. Its characters were substantially identical with English oil. Japanese dill oil appears to be produced from the same seed as the East Indian oil.

**DIMETHYL-BENZYL CARBINOL.**—This body,  $C_6H_5 \cdot CH_2 \cdot C(OH)(CH_3)_2$ , is an isomer of phenyl propyl (hydrocinnamyl) alcohol. It forms crystals melting at  $21^\circ$ , and boiling at  $225^\circ$ . It is prepared by the interaction of zinc methide and phenylacetyl chloride. It has an odour recalling that of narcissus, hyacinth and lilac, and is one of the rarer, but highly prized, synthetic perfumes.

**DIMETHYL-HEPTADIENE-OL.**—This body is one of most recently synthesised odorous compounds, formed by the condensation of mesityl oxide and bromopropyl acetate. It is an

oil, boiling at 78° to 80° at 18 mm. It possesses an intense odour of cedarwood, and yields an acetate having a similar odour. (Bogert and Slocum, *American Perfumer*, xviii., 12, 621).

**DIMETHYL-HYDROQUINONE.**—This body,  $C_6H_4(OCH_3)_2$ , the dimethyl ether of hydroquinone, is a crystalline body, melting at 56° and boiling at 205°. It has an odour of the new-mown hay type, and blends well with coumarin in flower odours, and is an excellent fixative.

**DIMETHYL-OCTENE-OL.**—This alcohol results from the interaction of acetobutanol and *i*-butyl magnesium iodide. It boils at 103° to 108° at 12 mm., and yields an acetate having a fine floral odour. An isomeric alcohol results from the condensation of aceto-propanol and *i*-amyl-magnesium iodide. It boils at 107° to 109° at 12 mm., and both it and its acetate have a fine odour resembling benzoin (Bogert and Slocum, *American Perfumer*, etc., xviii., 12, 621).

**DIMETHYL-PHLORACETOPHENONE.**—The essential oil of *Blumea balsamifera* and several of the xanthoxylum oils contain a small quantity of this ketone, of the formula  $C_6H_2(COCH_3)(OH)(OCH_3)(OCH_3)$ . It is an odorous crystalline substance, melting at 82° to 83°.

**DIMETHYL-THYMOHYDROQUINONE.**—This quinone ether is a natural constituent of the essential oils of *Armica montana* (*Annalen*, 170, 363) and *Eupatorium triplinerve*. It is an odorous oil having a specific gravity 0.991 at 20°; refractive index, 1.5134; and boiling point, 249°.

**DINITRO-BUTYL-*m*-CRESOL METHYL ETHER.**—This is the "musk ambrette" of commerce. It melts at 85°. (*Vide* "Musk.")

**DINITRO-BUTYL-*m*-XYLENE.**—The acetyl derivative of this body is ketone musk. It has a rich musk odour, and melts at 134° to 135°. (*Vide* "Musk, Artificial.")

**DINITRO-BUTYL-XYLYL-ALDEHYDE.**—This body is one of the least common artificial musks, known as "aldehyde musk." It is a crystalline compound, melting at 112°. (*Vide* "Musk.")

**DINITRO-BUTYL-XYLYL CYANIDE.**—This body is a comparatively rare artificial musk (*vide* "Musk"). It is a crystalline body, melting at 110°.

**DIOSPHENOL.**—Diosphenol, or buchu camphor,  $C_{10}H_{16}O_2$ , is a phenolic ketone, occurring naturally in certain of the buchu

leaf oils. It is a crystalline substance having the following characters: melting point,  $84^{\circ}$ ; boiling point,  $232^{\circ}$ ; and optical rotation,  $\pm 0^{\circ}$ . It has been artificially prepared by Semmler and Mackenzie (*Berichte*, 1906, **39**, 1158) by oxidising oxymethylene-menthone and inverting the resulting diketone with caustic alkali. Cusmano (*Att. R. Acad. d. Lincei*, 5, **22**, ii., 1913, 569) has also prepared it artificially by treating dibromo-menthone with caustic alkali and saturating the resulting liquid with carbon dioxide. Diosphenol, usually in the form of buchu oil rich in the ketone, is of value when used in very small amount in odours where a suggestion of black currant flowers and fruits has been introduced. It also gives a characteristic tone to flavouring essence of black currant. Diosphenol has also been prepared from piperitone (*q.v.*).

**DIPHENYL-KETONE.**—This body is generally known as benzophenone (*q.v.*).

**DIPHENYL-METHANE.** — Diphenyl-methane  $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$  is a very valuable synthetic perfume. Its odour is very powerful, and resembles that of geranium leaves, so that, in common with diphenyl oxide, it shares the name "artificial geranium." It is a hydrocarbon, and therefore very stable in the presence of free alkali, so that it is of considerable value in soap perfumery. It is a crystalline compound melting at  $26^{\circ}$  to  $27^{\circ}$ , and boiling at  $261^{\circ}$ . It is prepared by the action of zinc dust on a mixture of benzyl chloride and benzene, or by the condensation of benzene with formic aldehyde in the presence of a small quantity of sulphuric acid.

**DIPHENYL OXIDE.**—This body  $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{C}_6\text{H}_5$  is a crystalline compound which has come into considerable vogue as a synthetic geranium. Its odour is strongly geranium, with a suggestion of orange and hyacinth. It forms crystals melting at  $28^{\circ}$ , and boiling at  $258^{\circ}$  to  $259^{\circ}$ . It was originally prepared by Gladstone and Tribe by the distillation of phenol-aluminium. It can be prepared by the dry distillation of copper benzoate, or by digesting diazo-benzene sulphate with phenol. This body is a good example of the fact that bodies are produced by the chemist without their odour values being realised, unless the chemist happens to be a perfume expert. This body was discovered in 1899, and the chemist who prepared it reported that "it has an indescribable orange-like odour, but has not found any practical application." It was not until about fifteen years later

that its geranium odour was noticed, and it then rapidly became a commercial product. (See also *La Parfumerie Moderne*, 1923, 51.)

**DIPTERYX ODORATA.**—The highly fragrant seeds known as Tonkin or Tonka beans are derived from *Dipteryx odorata* and *Dipteryx oppositifolia*, large trees of the natural order *Leguminosæ*, natives of Cayenne. The former grows principally in Guiana, and the latter in Brazil. In British Guiana the tree is known by the natives as *Kuswara*. It grows (according to Sawer, "*Odorographia*," vol. i., p. 132) plentifully in some localities, especially above and on the islands in the rapids of the Esquibo River. The beans contain a fixed oil, which, when expressed, contains a certain amount of the perfume of the bean, and which is highly esteemed as a hair oil by the natives. This, it is suggested, may be the origin of the formerly well-known (so-called) hair restorer known as balm of Columbia. The tree also grows in Martinique.

According to Albes (*American Perfumer*, 1916, 10, 278), the best beans come from the region between the Caura and Cuchivero rivers, in eastern Venezuela, where the soil seems to be most favourable for the growth of the Tonka bean tree. The trees are not usually found in groves, but grow singly, though small clumps are occasionally met with. The gathering of the nuts is thus all the more difficult and arduous. Cultivation of the tree has been attempted in Trinidad and other parts of the West Indies, but as it takes from ten to twelve years for a tree to come into bearing, this has apparently discouraged the planters, and the wild product is still depended upon to supply the markets. The crops seem to be very irregular. As a rule, there does not seem to be more than one good crop in three years, production in the interval being so small that it hardly pays to collect the beans.

In Venezuela the tree is known as *sarrapia*, the men engaged in the collection of the seeds being called *sarrapieros*. Ciudad Bolivar is the centre of the Tonka bean industry.

Birds, especially of the parrot family, frequently cause considerable damage. They feed on the small immature fruit of the trees in the months of October and November, long before the beans are ready to be gathered. Where these birds have eaten the ground is strewn with fruit only clawed, and then awkwardly dropped, or perhaps with just a small piece bitten off.

About the beginning of February the *sarrapieros* begin to organise their expeditions to the interior to collect the beans. For two or three months thereafter the Caura River is animated with boats of every kind and description, some of them carrying

entire families on their way to the districts where the trees are found. As soon as a suitable place has been found, ranchos or huts are built, which are to be the *sarrapieros'* homes for perhaps two or three months. Once the fruit of the trees in the vicinity of the ranchos has been gathered, the men go farther into the forests, sometimes taking their supplies with them and remaining absent for a week or two.

The fruit of the Tonka bean tree resembles a mango in appearance; it has but little pulp, which is sticky and tasteless, but edible. The seed (or bean) is covered with a hard furry substance. After a sufficient quantity of the fruit has been gathered, it is taken to some open place, where it is further treated. The hard shell is carefully crushed between two stones, and the single oblong seed removed and dried in the sun. These dried seeds are the Tonka beans of commerce as they are sold to the merchants and exporters in Ciudad Bolivar. By the end of May or the beginning of June the crop is completed.

Before the beans are exported they go through a process of crystallising by being steeped in strong rum or alcohol. Casks open at one end are filled with the beans to within about a foot from the top. The rum is then poured in until the cask is full, when it is covered by layers of gunny bags. After twenty-four hours the rum not absorbed is run off, and the beans are spread out to dry in a current of air. When first taken out, the beans are of dark brown colour and are swollen with the absorbed fluid. On drying they shrink and become covered with coumarin crystals.

The tree reaches a height of 60 to 90 feet. The pods each contain one seed, shaped like an almond, but larger, and covered with a black shiny skin. When the seed is ripe, the seed pod does not open, as is usual with leguminous plants, but, when detached from the stem, rapidly acquires a powerful aromatic odour suggestive, when very dilute, of new-mown hay. This is due to the gradual development of about 3 per cent. of coumarin (*q.v.*), which may be seen in white crystals beneath the skin of the seed and between the lobes. The comparatively large amount of fixed oil present in the seed acts as a fixative, and prevents the coumarin from evaporating more than slowly, so that the beans retain their odour for a very long period. The beans are often found to be covered with a crystalline layer of coumarin, which is either natural on account of age, the coumarin having been gradually volatilised from the centre to the surface, or, by their having been steeped in rum and then laid out to dry as above described.

To prepare coumarin from the natural source the finely cut up material is boiled with 80 per cent. alcohol, the alcoholic solution filtered and concentrated, and the concentrate is mixed with four times its volume of boiling water. The solution is filtered through wetted filter paper to remove fat and oil, and then set aside to cool. The coumarin then crystallises out, and may be purified by recrystallising after dissolving in hot water and shaking with animal charcoal to decolourise. The so-called "Angostura" beans are the larger and more esteemed, the "Para" beans being smaller and of less fine odour. (*Vide* "Coumarin," and "Liatris odoratissima.")

**DISTILLATION, FRACTIONAL, IN ANALYSIS.**—The analysis of essential oils embraces the determination of as many characters as possible of the oil to be examined. Obviously, the greater the number of characters determined, all of which are compared with the known characters of authentic oils, the greater is the chance of coming to a correct conclusion as to whether the oil examined is genuine or not. This state of facts, however, is as well known to the dishonest adulterator as to the honest chemist, and the former is always endeavouring to keep a step in advance of the latter in order to confuse and mislead him. Endeavours are made to make mixtures which shall have the same specific gravity, optical rotation, refractive index, and other general characters as a pure essential oil has. It is obvious, however, that the greater the number of such characters to be determined, the less the chance of the adulterator deceiving the analyst is. Hence the necessity of multiplying the number of analytical characters to be determined to the greatest possible extent. This is most satisfactorily achieved by subjecting the oil to fractional distillation, and so separating the oil into fractions boiling at different temperatures, and therefore containing different constituents, and determining all the usual characters on all the fractions so obtained. Whilst a skilful adulterator may successfully imitate all the usually determined characters of an essential oil as a whole, it is a practical impossibility, except in very rare cases, for him to so compound an oil that, when it is separated into numerous fractions, all the fractions shall have the same characters as the corresponding fractions of the genuine oil.

In fractionating an oil, the character of the oil must be taken into consideration in determining the method of distillation to be employed. Many oils can be fractionated by distillation at ordinary pressure in either an ordinary Wurtz flask or in a three-



bulb flask, which effects a rather better separation. Further still, heads of various forms may be used, which effect a still better separation of the various constituents. Other oils must be distilled under reduced pressure, the pressure varying according to the nature of the constituents of the oil. But, whatever the conditions of fractionation, it is absolutely essential that they should be identical in the case of the sample under examination and the standard sample with which it is being compared.

To exemplify the value of this method of examining essential oils, the following examples may be quoted :—

The writer (E. J. P.) and Bennett have examined suspected oils of peppermint with the following results.

A pure American peppermint oil gave the following results, the fractions being collected in quantities of 12·5 per cent. as distillation proceeded :—

Fraction.	Specific gravity.	Rotation.	Refractive index.
1	0·898	— 10°	1·4660
2	0·903	— 14°	1·4635
3	0·907	— 16°	1·4645
4	0·910	— 20°	1·4640
5	0·912	— 23°	1·4615
6	0·912	— 23°	1·4615
7	0·915	— 34°	1·4630
8	0·962	—	1·4790

An oil which was suspected, and finally found to be adulterated with the artificial ester triacetin, was distilled under identical conditions, and the fractions examined, with the following results :—

Fraction.	Specific gravity.	Rotation.	Refractive index.
1	0·900	— 15°	1·4645
2	0·902	— 15°	1·4670
3	0·910	— 14°	1·4650
4	0·920	— 16°	1·4640
5	0·926	— 20°	1·4640
6	0·938	— 22°	1·4640
7	—	—	1·4640
8	1·147	—	1·4450

## P E R F U M E R Y

Without discussing the characters of any fractions but the last, it is obvious that the very high specific gravity and the very low refractive index pointed at once to adulteration with a high boiling liquid, of high specific gravity and a refractive index which, considered with the other characters, indicated the presence of an aliphatic body. Samples of sandalwood oil which, on the examination of the oil itself, gave no definite indications of adulteration, were similarly distilled fractionally. In this case nine fractions, each of 10 per cent., were collected, the remaining 10 per cent. being left as a residue in the distilling flask. A pure normal sample gave the following values :—

Fraction.	Specific gravity.	Rotation.	Refractive index.
1	0.977	— 18°	1.5078
2	0.964	— 17°	1.5038
3	0.969	— 16°	1.5051
4	0.975	— 15°	1.5068
5	0.979	— 15°	1.5072
6	0.980	— 14°	1.5078
7	0.981	— 16°	1.5083
8	0.981	— 18°	1.5083
9	0.978	— 22°	1.5086

A suspected sample gave the following results when separated into identical fractions under identical conditions :—

Fraction.	Specific gravity.	Rotation.	Refractive index.
1	0.965	— 5°	1.5036
2	0.967	— 5°	1.5048
3	0.972	— 4° 30'	1.5062
4	0.975	— 4° 30'	1.5075
5	0.976	— 5° 50'	1.5079
6	0.978	— 6°	1.5083
7	0.978	— 8°	1.5080
8	0.981	— 10° 10'	1.5090
9	0.983	— 14°	1.5095

The great difference in the optical rotation of the fractions at once reveals the presence of an adulterant. (See also under "Lavender Oil" for the fractionation of spike lavender oil.)

This method of examining essential oils is invaluable, and where there is some abnormality which renders the oil suspicious, but is not in itself sufficient to condemn it, fractional distillation will generally decide whether the oil is pure or not.

**DISTILLATION OF ESSENTIAL OILS.**—The distillation of essential oils may be conveniently divided into two sections, the first involving the scientific principles of steam distillation, and the second dealing with technical considerations, mainly consisting of the correct conditioning of the raw plant material before distillation, and its subsequent treatment.

It is first advisable briefly to deal with the more important theoretical aspects of the operation of steam distillation considered apart from the complications which arise in the winning of the oil from its natural source. These theoretical aspects deal with the phenomena obtaining in the distillation of completely immiscible liquids, in this case water and the essential oil, which, for convenience, is considered as a single substance.

The basic law on which the whole science depends is that enunciated by John Dalton in 1802. Dalton found that, when two or more gases or vapours which do not associate or react chemically with one another are mixed, each gas exerts the same pressure as if it alone were present, and that the sum of the "partial" pressures is equal to the total pressure exerted by the mixture.

It is necessary thoroughly to grasp this conception, and it may assist if it be stated in another way, viz.: The volume occupied by a mixture of gases or vapours is equal to the sum of the volumes which the component gases or vapours would occupy at the same temperature and pressure.

The saturated—*i.e.*, not superheated—vapours of liquids which are completely immiscible with one another follow Dalton's law, the vapour pressure of the mixture being the sum of the vapour pressures of the constituents of the mixture, and it is important to note that the total pressure is not influenced by the relative amounts of the constituents, *i.e.*, water and essential oil.

If a mixture of immiscible liquids be distilled, the temperature at which boiling takes place, in the absence of superheating, is that at which the sum of the vapour pressures is equal to the external pressure on the system (*e.g.*, the atmospheric pressure). Each liquid, considered separately, is consequently boiling at a lower temperature than it would in the absence of the other liquid, and this temperature is the same for all the constituents.

The vapour coming from such a boiling mixture contains all the constituents in proportion by volume to the relative vapour pressure of each, and the distillate contains all the volatile ingredients of the original mixture.

*Steam Distillation at Ordinary Pressure.*—If  $P_a$  and  $P_b$  are the vapour pressures of two immiscible liquids A and B at  $t^\circ$ —e.g., water and essential oil—the two substances will distil over in the proportion  $\frac{P_a}{P_b}$  by volume of vapour. If  $D_a$  and  $D_b$  are the respective vapour densities at the boiling point of the mixture, the relative quantities by weight  $W_a$  and  $W_b$  will be expressed by:

$$\frac{W_a}{W_b} = \frac{P_a D_a}{P_b D_b}.$$

The molecular weight of a substance is equivalent to twice its vapour density, i.e.,  $M = 2D$ ; hence we can write the equation:

$$\frac{W_a}{W_b} = \frac{P_a M_a}{P_b M_b};$$

whence it follows that the mixed vapour will consist of:

$$\frac{P_a M_a}{P_a + P_b} \text{ of A and } \frac{P_b M_b}{P_a + P_b} \text{ of B.}$$

If we consider 1 litre of the mixed vapour, this will contain 1 litre of the vapour of each component—according to Dalton's law—at its particular partial pressure, and the weight of each of these will be respectively:

$$\frac{0.0896 \times M \times 273 \times P}{2 \times 760(273 + t)}.$$

From this we can calculate, with sufficient accuracy for our purpose, the amount of water that is necessary to steam-distil over a given quantity of a substance. Thus in the case of benzaldehyde, which is the chief constituent of oil of bitter almonds, its molecular weight is 106, its vapour pressure at  $100^\circ \text{C.}$  is 61 mm.; consequently the partial pressures of water and benzaldehyde at atmospheric pressure and  $100^\circ$  are given by:

$$P_a = \frac{P'_a \times 760}{P'_a + P'_b} = \frac{760 \times 760}{760 + 61} = 703.5 \text{ for water}$$

and

$$P_b = \frac{P'_b \times 760}{P'_a + P'_b} = \frac{61 \times 760}{760 + 61} = 56.5 \text{ for benzaldehyde,}$$

the two partial pressures, 703.5 and 56.5, totalling to the atmospheric pressure, 760. Substituting in the second equation quoted, we get :

$$\frac{W_a}{W_b} = \frac{M_a P_a}{M_b P_b} = \frac{18 \times 703.5}{106 \times 56.5} = \frac{68}{32},$$

that is, the distillate will consist of 32 per cent. of benzaldehyde and 68 per cent. of water.

The statements made above refer to steam distillation carried out under ordinary atmospheric pressure. Other pressures, either greater or less, may be employed, as also may be superheated steam; further, the oil itself may be superheated, provided it is not deleteriously affected by such treatment. Generally, the effect of increasing the temperature or the pressure is to increase the proportion of essential oil relatively to the water; hence, these alternatives may be usefully employed when dealing with stable bodies, but they are quite unsuited to the more delicate essential oils, especially those containing esters or aldehydes in any considerable proportion. For such, the use of diminished pressure and low temperature is advisable, provided the duration of the distillation be not thereby unduly prolonged.

*Distillation with Superheated Steam.*—We will first consider the effect of increasing the temperature of the ingoing steam. If water be boiled in a boiler, the temperature of the steam varies with the pressure, and if the steam thus generated be allowed to issue from the boiler into a still worked at some pressure below that of the boiler (*e.g.*, atmospheric), the temperature of the steam drops owing to the work done in expanding. The table on p. 190 indicates this drop in temperature in passing from the given boiler pressures to atmospheric or one-tenth atmospheric pressure.

The drop in temperature may be calculated by means of Zeuner's equation :

$$pv = BT - Cp^n,$$

where B, C and  $n$  are constants, and  $\frac{C}{B} = 38.11$ ;  $n = 0.25$ ;

$p$  = the pressure in atmospheres;  $v$  = the volume in cubic metres per kilogram;  $T$  = temperature in degrees centigrade.

If the steam in a boiler at temperature  $T_1$ , absolute pressure  $p_1$ , and volume  $v_1$ , be released into a still at  $T_2$ ,  $p_2$ ,  $v_2$ , respectively, then

$$p_1 v_1 = p_2 v_2 = BT_1 - Cp_1^n = BT_2 - Cp_2^n.$$

whence

$$T_1 - T_2 = \frac{c}{B} (p_1^* - p_2^*).$$

Thus, if a boiler gauge register 56 lb. per square inch, corresponding to 5 atmospheres absolute pressure, and the steam be injected into a still at normal atmospheric pressure, from the above table we find :

$$152.2 - T_2 = 38.11 (5^{0.25} - 1^{0.25}),$$

whence  $T_2 = 133^\circ \text{C}.$

Similarly, if  $p_2 =$  one-tenth of an atmosphere, then  $T_2 = 116^\circ \text{C}.$  Thus the temperature of the steam drops from  $152^\circ$  to  $133^\circ$  or

Boiler pressure, lb. per sq. inch.*	Initial temperature.	Temperature after expansion to	
		one atmosphere.	one-tenth atmo- sphere.
0	100° C.	100° C.	83.3° C.
7	111.7	108.1	91.4
14	120.6	113.4	96.7
28	133.9	121.9	105.2
42	144.0	128.2	111.5
56	152.2	133.3	116.6
70	159.2	137.7	121.0
84	165.3	141.4	124.7
98	170.8	144.8	128.1
112	175.8	147.9	131.2
126	180.3	150.7	133.9

\* This is the reading on the boiler pressure gauge, and does not include the 14 lb. due to the atmosphere.

$116^\circ$  when injected into a still under atmospheric pressure or one-tenth of atmospheric pressure respectively. In spite of this drop in temperature, the steam contains more heat than it would if it had been generated under ordinary pressure—for instance, by boiling water in the still itself. In this latter instance, the temperature would be  $100^\circ \text{C}.$  instead of  $133^\circ$ ; hence the steam is said to be superheated or unsaturated. Steam may also be superheated by passing it through pipes heated by an external source of heat, and a much greater degree of superheat may be obtained in this manner, both these devices merely serve the purpose of enabling the steam to transfer more heat than it

otherwise would. The use of superheated steam has another advantage, that there is less condensation due to radiation, the superheat of the steam causing any condensed water to evaporate ; so long as liquid water exists in the still, the advantage of the superheating is lost. If all condensation of steam is prevented, the higher temperature of the superheated steam tends to increase the proportion of oil in the distillate ; the same effect may be obtained by heating the oil to a temperature above that of the ingoing steam.

*Steam Distillation under Increased Pressure.*—As an alternative to either of these methods, we may conduct the distillation under pressures higher than atmospheric. This is done by interposing a weight or spring loaded valve between the still head and the condenser ; the method is not, however, in common use.

The effect of the pressure in the still is reflected in the following figures obtaining for benzaldehyde :

Pressure.	Temperature.	Benzaldehyde.
$\frac{1}{10}$ atmosphere	45·3° C.	22·5 per cent.
1            ,,	97·9	31·4    ,,
4            ,,	140·7	38·2    ,,

It will be seen that, whereas the proportion of benzaldehyde is increased, the increase in the temperature to which it is submitted is very considerable ; this for many substances is prohibitive.

*Steam Distillation under Diminished Pressure.*—In order to reduce the temperature of the distillation, diminished pressure may be resorted to, this, as is indicated in the table above, also results in the percentage of the less volatile constituent, *e.g.*, benzaldehyde, being diminished ; there is a further drawback, inasmuch as there is considerable difficulty in condensing the vapours produced. For essential oils of a delicate nature, *e.g.*, lavender, neroli, the method is to be recommended, but in view of the technical difficulties involved, it is not usual to resort to pressures below one-tenth of an atmosphere.

Steam distillation with superheated steam under diminished pressure also offers advantages.

*The Heat of Distillation.*—The amount of heat—and hence fuel—necessary for the steam distillation of a given quantity of an essential oil can be roughly calculated, but it is necessary to know

the amount, the vapour pressure at 100° C., and the molecular weight of each constituent of the essential oil. The amount of steam necessary for each constituent has first to be ascertained; this can be calculated from the molecular weight of the substance and its vapour pressure at 100° C., as has already been shown.

From the figures thus obtained, the amount of heat necessary to vaporise each ingredient, including the water, can be found, the total heat being the sum of all these. The heat of vaporisation, *H*, may be calculated from the change of vapour pressure with change of temperature, using the formula :

$$H = \frac{dP}{dT} \cdot \frac{1.985 T^2}{P},$$

where *T* is the absolute temperature at pressure *P*, and *dP* the small rise in pressure caused by the small rise in temperature *dT*.

Thus, in the case of cymene, which has a boiling point of 174° C.—i.e., (174 + 273)° absolute—at the normal pressure of 760 mm. : for every 1 mm. increase in *dP*, there is an increase of 0.057° in *dT*, and the heat of vaporisation at atmospheric pressure is given by

$$H = \frac{1}{0.057} \times \frac{1.985(174 + 273)}{760} = 9156$$

calories per molecule.

Experimentally, the value has been found to be about 2 per cent. lower, i.e., 8978 calories per molecule. By dividing this value by the molecular weight of cymene (134), the heat of vaporisation for 1 kg. is given as 68.

The following data have been published concerning the heat of vaporisation of bodies which occur in essential oils :—

Substance.	Temperature.	Heat of vaporisation.	
		One kilogram.	One kilogram molecule.
Acetophenone . . .	203.7° C.	77.2	9.3 × 10 <sup>3</sup>
Anethole . . .	—	71.5	10.6 „
Benzaldehyde . . .	—	86.6	9.2 „
Cymene . . .	175	67.0	9.0 „
Carvacrol . . .	—	68.1	10.2 „
Turpentine . . .	159	69.0	9.4 „
Water . . .	100	536	9.6 „



*Dry Distillation.*—Very few essential oils can be dry distilled, *i.e.*, without water or steam, at ordinary pressure without undergoing serious decomposition, on account of the high temperature that it is necessary to employ. In order to avoid this high temperature, resort may be had to the use of diminished pressure, or as it is commonly termed, a vacuum.

The problem now involves a consideration of the distillation of liquids miscible in all proportions. Only the simplest case will be dealt with here, namely, that of a mixture of two liquids which do not associate or react with one another and which, in consequence, follow Dalton's law.

If  $V_a$  and  $V_b$  be the vapour pressures of two such liquids A and B, and these be mixed in the proportion of one molecule of A to  $n$  molecules of B, then the partial pressures  $P_a$  and  $P_b$  of the two substances are such that :

$$P_a = \frac{V_a}{1 + n} \text{ and } P_b = \frac{V_b}{1 + n}.$$

The total vapour pressure  $P$  of the mixture is given by ;

$$100 P = M_a P_a + (100 - M_a) P_b,$$

where  $M_a$  is the molecular weight of A.

By means of this formula it is possible to calculate the vapour pressures of mixtures of two substances at any pressure. Quite accurate results are obtained, except in the case of liquids which associate with one another ; these are, however, apparently of rare occurrence in essential oils.

When a mixture of two non-associating, miscible liquids is heated to boiling, the vapour which arises is richer in the more volatile component than is the liquid ; hence, as distillation proceeds, the *proportion* of the *less* volatile component increases in the liquid until all of the more volatile has been removed. (The more volatile component is, of course, that having the lower boiling point.) It follows that the vapour has a higher proportion of the more volatile component, and if this vapour be condensed and submitted to a fresh distillation, a further separation of the mixture into its two components is similarly effected ; by repeating this series of operations a sufficiently large number of times, a more or less complete separation may be effected, and this, in effect, is the action of a fractionating column.

Fractionating columns are only resorted to in the case of essential oils, when it is desired to isolate some particular constituent or to remove undesired bodies, and it must be borne in mind that the repeated boiling and condensing, upon which the

action of such columns depend, tend deleteriously to affect the oils.

*The "Winning" of Essential Oils.*—The considerations set out in the preceding sections concern the oil after it has been released from the plant in which it occurs in the natural state. When the oil has to be distilled out of the plant, a further factor is involved, namely, the rate at which the plant parts with its essential oil. This rate may be so slow that the other factors, such as vapour pressure, are swamped completely, and it is therefore of prime importance to reduce as far as possible the "lag" thus occasioned. In order to accomplish this, it is necessary to submit the plant to some suitable breaking-up process, but in some instances, such as geranium, lavender, rosemary, the lag is so small that it can be neglected and no preliminary treatment given to the plant. The treatment varies with the nature of the material; thus berries may be crushed, seeds and roots ground, wood chipped, twigs and branches cut, and so on. When submitting the raw material to any preliminary treatment, it is well to bear in mind that exposure to heat and air tends to cause loss of oil through evaporation and oxidation.

Two methods of distillation are widely practised, namely, distillation by boiling with water (water distillation), and distillation by the injection of steam (steam distillation). The former is employed on account of its convenience and the simplicity of the necessary apparatus, but the latter, which in general gives the better product, is employed in the larger distilleries almost exclusively.

The apparatus may be constructed of almost any convenient metal, copper being usually preferred; wood is also often employed for the still body. The precise shape and size of the still is not of great importance; cylindrical stills are the most common. The material to be distilled is usually supported on a perforated false bottom, in order to keep it from direct contact with the hot bottom or steam coils, as the case may be, such contact tending to cause destructive distillation, with the consequent production of evil smelling-bodies. Instead of a perforated false bottom a gauge basket is sometimes employed, the spent charge being removed by lifting the basket out of the still after taking off the cover.

The vapours coming from the still are condensed by passage through a spiral coil immersed in a tank of running cold water, or by means of special condensers, such as the "Ideal," in which

the vapour is caused to pass between narrow annular spaces formed by fixing, concentrically, one tube inside another of slightly larger diameter, a wire being wound spirally in the space between the two tubes.

The liquid issuing from the condenser consists of a mixture of oil and water; usually the oil is lighter than water, and in course of time floats out—occasionally, however, it or some fraction of it is heavier and sinks; the two layers are separated automatically by means of “essenciers,” which consist of vessels having overflow tubes arranged at suitable heights. In the case of some oils, considerable difficulty is experienced in obtaining a good separation of oil and water owing to emulsification, the water remaining cloudy, even after standing many hours. There are three common methods for dealing with this difficulty: (1) returning the cloudy water to the still instead of supplying fresh water or steam (cohobation); (2) extracting the water with an immiscible solvent, such as benzene; (3) passing the water through some material which will absorb the oil, such as kieselguhr or sawdust, and then subsequently steam distilling the mass.

When the oil has eventually been separated from the mass of the water, it should be dried by filtering or by setting aside in a cool place until clear, placed in well-closed, suitable packages, *e.g.*, bottles, tinned copper or tinned iron containers, and stored in a cool place; careless treatment of the oil may result in rancidity, lack of sweetness, or bad colour.

T. H. D.

**DISTILLED WATERS.**—A certain number of essential oils contain sufficient highly aromatic constituents which are soluble in water to such an extent that they impart to the distillation water an odour which makes the water sufficiently aromatic to be of considerable value to the perfumer. In general, however, the situation of the distillery and the conditions of the distillation, coupled with economic considerations, such as the disproportionate freights for the conveyance of a comparatively cheap article, are such as to make the trade in such aromatic waters either impossible or unremunerative. It is, of course, only a few oils which yield distillation waters of any value. Where the process is possible, distillation waters which contain dissolved essential oil, and which are not saleable as such, are, as far as possible, returned to the still so that a further loss of oil, which would take place if fresh water were used, is thus avoided. The principal distilled waters which form commercial articles are rose water and orange flower water. Such waters are usually sold under a conventional name

as to concentration, such as "aqua rosæ triplex." Such terms are more or less arbitrary, as they do not indicate that, for example, 3 lb. of flowers have been distilled for 1 lb. of the water, but that, for example, it is an early fraction of the distillation water, so that considerable dilution has not taken place. It is obvious that the distillation water and the essential oil itself will not have identical odours, as their odour is not due to identical constituents. For example, phenyl-ethyl alcohol is a regular constituent of the rose flower. This alcohol is comparatively soluble in water, so that it is substantially absent from otto of rose (the essential oil of the rose), whilst it is responsible for the characteristic odour of rose water. Apart from the two waters mentioned above and a very few others, such as cherry laurel, the bulk of so-called aromatic waters are made by dissolving a very small amount of essential oil in a little alcohol and pouring this into a large volume of water, which is well agitated and eventually filtered, if necessary, with the aid of filtering powder. (See also "Rose Water" and "Orange Flower Water.")

Guyot (*Jour. de Pharm. et de Chim.*, vii., 1916, 13, 37) has investigated the cause of the green discoloration which often takes place in perfumed and medicinal waters. The following are, according to Schimmel & Co. (*Report*, 1916, 39), Guyot's conclusions :—

"The coloration is due to an aerobic microbe forming colourless clusters of rod-like organisms, 4 to 5  $\mu$  long and 0.5  $\mu$  wide, which are coloured by basic aniline dyes and methyl blue, and assume the Ziehl and Gram colorations. This microbe is different from *Bacillus liquefaciens fluorescens* and from most water bacteria producing green fluorescence. It produces a green non-fluorescent coloration. It also differs from *Bacillus pyocyaneus* as well as from Lesage's bacillus. The new microbe appears to be able to exist without giving off the green colour; its colour-forming properties are dependent upon extraneous surroundings and the composition of its cultivating solution. Oxidising media and oxygen favour the development of the green coloration, while reducing substances weaken it and make it disappear entirely. Light has a favourable influence on the development of the green colour. Zinc acts as a reducing substance; this is the reason why green coloration does not take place with orange flower water stored in zinc vessels. An alkaline reaction of the liquid favours the development of the microbe.

"The green colouring matter evidently belongs to the group of

aurantiachlorines ; it is insoluble in alcohol, methyl alcohol, ether, chloroform, and benzene, but dissolves in water. To isolate the colour, undyed wool is immersed in the liquid when the colour is precipitated on the wool. If the wool is treated with diluted acids, the green colour is converted into a brick-red one, soluble in alcohol, methyl alcohol, ether, chloroform, and benzene. If this solution is neutralised, the red colour is once again converted into the green colour, soluble in water. Cherry laurel water never shows green coloration. No decrease in odour is noticeable in the waters owing to the change involved by the green coloration ; on the contrary, with orange flower water, for instance, the opposite effect may be observed."

Juillet (*Roure-Bertrand Fils, Bulletin*, October, 1913, 22) has carried out an investigation on the methods of preserving distilled waters and preparing them in a sterile condition. The following is an outline of his historical *résumé* of the question :—

These waters are exceedingly unstable preparations ; their alterations are sometimes of a physico-chemical order (evaporation of certain active principles, oxidation of essential oils, etc.), sometimes of a biological nature (attacks by fungi or algæ). Consequently the question of their preservation has for a long time occupied the attention of pharmacologists, and, while not presuming to recapitulate here all the history of the problem, it seems to me of interest to mention its main outlines.

At the beginning of the last century there was at first a belief (Bahoff and Deyeux) in the transformation of the essential oil into mucilage, a fact which appeared to be demonstrated to the authors by the observation of the presence of " mucilage " in the watery extracts obtained artificially by dissolving an essential oil in water.

Soubeiran was the first to recognise the organised structure of these supposed mucilages, which Biasoletto shortly afterwards (1832) classified among the algæ of the genus *Hygrocrocis*. Later, L. Marchand (1878 and 1883) and other observers showed that these *Hygrocrocis* are fungi, the abnormal forms of which are the result of the special conditions of existence to which they are subject in the watery extracts. The study of these micro-organisms was the subject of investigations carried out by Tulasne, de Barry, Thuret, Bornet, and van Tieghem ; and in 1896 Barnouvin, returning to the question, classified them in order of importance among the fungi, the bacteria and the algæ.

The fungi, by far the most frequent, had first been classed in

the genus *Hygrocrocis*; but it is well recognised at the present day that the latter really comprises different genera, the characters of which are profoundly modified by the composition of the media in which the plants live. The most abundant and the most frequent is *Penicillium glaucum*, then come *Aspergillus* and *Sterigmatocystis* species; the group of the *Dematia* is also very largely represented by various species of *Cladosporium*, *Dematium*, *Alternaria*, to which must be added *Cephalosporium*, *Fusarium*, *Mucor*, etc. Many of these fungi may occur under these conditions as yeast-like forms, and even may only affect this form in certain watery extracts.

The bacteria are, as a rule, of the genera *Leptothrix*, *Micrococcus* and *Bacillus*, with numerous chromogenic species (*B. aurantii*, *B. fluorescens*) capable of communicating to the distilled waters in which they grow the colour of their pigments.

The algæ are unicellular, and belong to the genera *Protococcus*, *Hematococcus* and *Coccochloris*.

These various organisms may, moreover, coexist in one and the same water. But, whether they are alone or associated, they always provoke profound modifications in the distilled waters infected by them.

The changes of a physico-chemical order necessarily vary with the nature of the active principle predominant in the water. Thus cherry laurel water may lose by evaporation a portion of its hydrocyanic acid, whilst by oxidation its essential oil may be converted into benzoic acid; under the same influence the essential oil dissolved in orange flower water is converted into acetic acid, and cinnamic acid is constantly present in cinnamon water.

Numerous attempts have been made to remedy these inconveniences, and proposals have been made, one after another, for filtration, chilling, heating, sterilisation by Appert's method, preservation in full bottles, well corked and in cool dark places, the addition, often unsatisfactory, of alcohol, etc., means more or less palliative, the effects of which are often contradictory and always insufficient.

Juillet describes in detail the best method of sterilising the stills used, and shows that filtration through Chamberland filters is of extreme value in rendering these waters sterile, and, if they are kept under suitable conditions after having been sterilised, they will remain unchanged for a considerable time. For details, the original paper should be consulted.

**DITTANY OIL.**—The herb *Cunila organoides*, one of the North American *Labiatae*, yields 0·7 per cent. of a reddish-brown oil resembling thyme in odour. It has a specific gravity 0·915, and contains about 40 per cent. of phenols, probably mostly thymol.

**DJAMBOL LEAF OIL.**—The leaves of *Psidium Guajava*, one of the *Myrtaceae*, a tree indigenous to tropical America, yield about 0·36 per cent. of essential oil of specific gravity about 1·069, and boiling at 237°. *Schimmel & Co.* have distilled some leaves from Santiago de Cuba, and obtained 0·2 per cent. of an aromatic oil having the following characters :—

Specific gravity	. . . . .	0·9157
Optical rotation	. . . . .	— 10° 5'
Refractive index	. . . . .	1·4964
Acid value	. . . . .	2
Ester value	. . . . .	6·4

**DOREMA AMMONIACUM.**—See “Ammoniacum.”

**DOREMONE.**—This body is a ketone of the formula  $C_{15}H_{26}O$ , occurring in the essential oil of ammoniacum. It has a specific gravity 0·8765 at 20°; optical rotation, + 3° 30'; refractive index, 1·4716; and boiling point about 150° at 12 mm. On reduction with sodium and alcohol it yields the corresponding alcohol, doremol  $C_{15}H_{27}OH$ , which has the following characters: specific gravity, 0·870; optical rotation, + 3°; refractive index, 1·4713; and boiling point, 145° to 150° at 12 mm. It is present in the oil in the form of its acetic ester. The ketone, alcohol and ester are all odorous liquids.

**DORYPHORA SASSAFRAS, OIL OF.**—The leaves of *Doryphora sassafras* have been found by Penfold (*Jour. and Proc. Royal Soc. N.S.W.*, lv., 270) to yield up to 0·85 per cent. of essential oil of a deep yellow or brown colour, with a marked odour of safrol. Two samples were examined, one from leaves gathered at Monga, the other from Currowan. They had the characters given in the table on p. 200.

**DOUGLAS FIR OIL.**—This oil requires a good deal of further examination. The reports made by Brandel and Sweet and by Schorger on oils stated to be derived from the leaves of the Douglas pine, and botanically described as *Pseudotsuga taxifolia*, indicate an oil of no particular perfume value. Schorger gives the following as the approximate composition of the oil:  $\alpha$ -pinene, 25 per cent.;  $\beta$ -pinene, 48 per cent.; dipentene and limonene, 6 per cent.; furfural, traces; esters, 6·1 per cent.;

free borneol, 6·5 per cent; and a green oil of unknown constitution, 3 per cent.

According to Henry and Flood (*Proc. Roy. Irish Acad.*, May, 1920) this tree is *Pseudotsuga glauca*, whilst the Oregon Douglas fir is the true *Pseudotsuga taxifolia*. These authors give the details of the examination of the oils distilled from the leaves of both trees grown in England, by C. T. Bennet, who reports as follows upon them. The oil from the leaves of the Oregon Douglas fir was distilled from 50 lb. of the leaves from trees growing at Buckhold, Berks. The yield was 0·11 per cent., and the oil had the following characters: specific gravity, 0·876; optical rotation,  $-7^{\circ}$ ; refractive index, 1·4835; and ester content, 12·4 per cent. He stated that the ester value was much lower than that of the

	Monga.	Currowan.
Specific gravity . . .	1·021–1·031	0·981
Optical rotation . . .	$+16^{\circ}$ to $+22^{\circ}$	$+28^{\circ}$
Refractive index . . .	1·5058–1·5091	1·4898
Ester number . . .	33	49
Safrol . . . . .	60–65 per cent.	30 per cent.
Camphor . . . . .	10–15 „	30 „
Pinene . . . . .	10 „	10 „
Sesquiterpene . . .	10 „	—
Eugenol . . . . .	1 „	3·5 „
Eugenol methyl ether .	—	Present.

Colorado Douglas fir oil, but that the odour was much more fragrant. The oil contains dipentene or limonene, but no, or only traces of, pinene. An appreciable quantity of geraniol was separated on fractionation, and it is to this that the aromatic odour appears principally to be due. By acetylation 31·5 per cent. of alcohols was indicated. Bornyl acetate somewhat masks the geraniol odour of the oil. Citral is present in traces. The oil from the Colorado Douglas fir was distilled from leaves from trees grown in East Liss, Hampshire. The yield was 0·31 per cent. of an oil having the following characters: specific gravity, 0·905; optical rotation,  $-46^{\circ}$ ; refractive index, 1·4717; and esters, as bornyl acetate, 34·5 per cent. The terpenes present consist mainly of pinene. The odour is due principally to the bornyl acetate present. (See also "Pine Needle Oils.")

**DRYOBALANOPS AROMATICA, OIL OF.**—The so-called Borneo camphor tree is a native of Sumatra and north-west



Borneo. Camphor as first known in this country (Arabic *Kafur*, Sanscrit *Kapura* = a pure white substance) was brought from the land known as Kaisûr, the present Sumatra, and was the product of *Dryobalanops Camphora*, a splendid forest tree growing in abundance in Borneo and on the west and north-west coasts of Sumatra. This substance, however, is now known to be borneol, and not true camphor. According to Sawer ("Odorographia," vol. i., p. 334), the borneol can only be obtained by the destruction of the trees, all of which do not contain borneol. Many of them only contain an essential oil which has not yet developed any borneol. Practically all the borneol obtained from these trees is used locally or exported to China, either for incense or embalming purposes. Several of the Russian pine needle oils are so rich in borneol or its esters that competition with such oils is out of the question. The essential oil has a specific gravity 0.918; optical rotation,  $+11^{\circ}$ ; and refractive index, 1.4885. Oils of low specific gravity have been deprived of borneol.

**DUODECYL ALCOHOL.**—This body has the formula  $\text{CH}_3(\text{CH}_2)_{10}\text{CH}_2\text{OH}$ , and is used in minute proportions in rounding off floral odours. It is a liquid boiling at  $257^{\circ}$ , crystallising at low temperatures, and melting at  $14^{\circ}$ . It is also known as lauric alcohol. Its specific gravity is 0.831 at  $24^{\circ}$ .

**DUODECYL ALDEHYDE.**—See under "Aldehydes, Higher Fatty."

**EAU DE COLOGNE.**—EAU DE COLOGNE is one of the most popular toilet perfumes—probably *the* most popular—in the world. It is not, of course, intended to give formulæ for any perfume in this work, but the general characters of this almost universally used water may be indicated. The original eau de Cologne was in all probability actually invented in the town of Cologne by one Jean-Marie Farina, who was born at Sainte Marie Majeure, in Italy, and went to Cologne to trade in perfumes, and invented this famous blend in 1709. Another version of its original manufacture is that it was first placed on the market by one Paul de Feminis in Milan, and was afterwards made in Cologne from 1690. The secret was then passed on to his nephew, Jean-Antoine Farina, who started manufacturing it in Paris. Whichever version is correct, there is no doubt that from the commencement of the eighteenth century eau de Cologne has been a very popular perfume, and many rival manufacturers, both in Cologne and elsewhere, have carried on its manufacture. The

trade name "Farina" proved somewhat of a stumbling-block to rivals to the original maker, but they found it easy to import members of the Farina family to Cologne, and so became entitled to use the name. Endless lawsuits have taken place in regard to the matter, and it is not very easy to say whether any maker to-day uses the original recipe. Le Maout satirically wrote the following quatrain on the "Farina" position in Cologne:—

Il<sup>s</sup> étaient deux alors : ils sont mille aujourd' hui  
 Sur ses temps primitifs le doux progres à lui,  
 Et chaque jour le Rhin vers Cologne charrie  
 De nombreux Farinas, tous 'seul,' tous Jean-Marie.

Eau de Cologne is in substance the product of Italian essential oils, mixed with one or two others, which certainly are not German. It is so delicate a perfume that only the finest alcohol should be used for its preparation—so much so, that this fact has given rise to the name "Cologne spirit," which indicates the highest grade of alcohol for perfumery purposes. The finest Eau de Cologne is that produced, not by the mere mixing of the ingredients, but by distilling the alcohol with most of the ingredients, and adding certain ingredients after the distillation. The longer the perfume is allowed to mature—up to one year—the better it will be. Hundreds of formulæ have been published for this perfume, but the following is sufficient to indicate its general characters. The bulk of the ingredients, in which bergamot oil should prevail, and which include lemon and orange oils, with a little lavender oil and orris root, are macerated with alcohol for several days, and then carefully distilled without the application of naked heat. To the distillate neroli oil, a very small amount of rosemary oil, and a trace of a fixative such as benzoin, are then added, and the whole allowed to mature for as long as possible. Where a cheaper eau de Cologne is desired, the oils are merely mixed with the alcohol, without distillation, often in the form of terpeneless oils. Numerous formulæ, which as a rule are merely indicative, as obviously valuable trade secrets rarely leak out, will be found in any of the text-books of practical perfume making.

**EGLANTINE.**—This well known "fancy" perfume is invariably based on one or other (or mixtures) of the three esters—methyl phenylacetate, butyl (or isobutyl) phenylacetate, and isobutyl benzoate.

**ELECAMPANE OIL.**—The root of *Inula Helenium*, a plant of the natural order *Compositæ*, yields from 1 to 3 per cent. of a

semi-solid essential oil, having an odour which recalls that of ladanum. This oil liquefies at from 30° to 45°, and has a specific gravity, 1.015 to 1.038 at 30° (melted); optical rotation, + 123° 45'; refractive index, 1.5221; acid value, 6 to 8; ester value, 160 to 180; and ester value after acetylation, 199. The oil consists almost entirely of an anhydride, named alantolactone,  $C_{15}H_{20}O_2$ , also known as helinin. This is a crystalline compound, melting at 76°, and boiling at 275°.

**ELEMI.**—See “Canarium Resins.”

**ELEMOL.**—This substance is a crystalline sesquiterpene alcohol, isolated from the essential oil of Manila elemi, by *Schimmel & Co.* It is the principal ingredient of elemi oil, to which it owes its fixative properties.

Jarnsch and Fautl (*Berichte*, 1923, 56, 1363) have shown that elemol is a bicyclic sesquiterpene alcohol, which is isomerised to a liquid alcohol by benzoylation. They term the crystalline body  $\alpha$ -elemol and the liquid body  $\beta$ -elemol. Pure  $\alpha$ -elemol  $C_{15}H_{26}O$  forms fine needles melting at 46°, and boiling at 142° to 143° at 10 mm.  $\beta$ -elemol has a specific gravity 0.9419 at 18°; refractive index, 1.5070 at 18°; and boiling point, 143° to 144° at 10 mm.

**ERIOSTEMON CROWEI, OIL OF.**—According to Penfold and Morrison (*Jour. and Proc. Roy. Soc. N.S.W.*, lvi., 227) the leaves and terminal branchlets of this plant (previously described as *Crowea saligna*) yield about 0.4 per cent. of essential oil having a safrol-like odour. The oil has the following characters:—

Specific gravity . . . . .	1.109–1.124
Optical rotation . . . . .	$\pm 0^\circ$
Refractive index . . . . .	1.5302–1.5321

The oil contains a little pinene, but contains about 90 per cent. of a phenol ether, which has been named croweacin. Two preparations had the following characters:—

Boiling point at 10 mm. . . . .	130–131°	130–132°
Boiling point at 766 mm. . . . .	—	256–258°
		(uncorrected)
Specific gravity . . . . .	1.1339	1.1298
Optical rotation . . . . .	$\pm 0^\circ$	$\pm 0^\circ$
Refractive index at 20° . . . . .	1.5330	1.5328

Its formula appears to be  $C_{11}H_{12}O_3$ .

true that the ester determination affords a fairly accurate basis for valuing oils distilled from plants grown in the same neighbourhood.

The esters in an essential oil are determined in the following manner. From 2 to 5 grams of the oil, according to the amount of esters expected to be present, are weighed into a small flask of about 250 c.c. capacity, and 10 c.c. of alcohol and a few drops of phenolphthalein solution added. Semi-normal solution of caustic potash in alcohol (of approximately this strength) is added drop by drop until the free acids present in the oil are neutralised. Twenty-five cubic centimetres of the alkaline solution are then added and the liquid boiled under a reflux condenser for one hour. A "blank" test, that is, 25 c.c. of the alkaline solution without the oil, is carried out at the same time. The contents of the flasks are then diluted with 100 c.c. of water and titrated with semi-normal hydrochloric or sulphuric acid. The difference between the two titrations gives the amount of alkali that has been used for decomposing the ester present in the oil. Not more than about half the alkali used should have taken part in the reaction. If substantially more than this has been used up, the determination should be repeated, using either less of the sample or more of the alkaline solution. The number of milligrams of KOH used to saponify 1 gram of the oil is termed the ester number. From this value the percentage of esters, expressed in terms of any given ester, can be calculated from the formula  $\frac{M \times A}{560} =$

percentage of ester, where M is the molecular weight of the ester and A is the ester number.

In order to save tedious calculations, a table has been prepared by *Messrs. Schimmel & Co.* which gives the amount of esters for every value usually obtained, in terms of the usually occurring esters, such as linalyl acetate, citronellyl acetate, sesquiterpene alcohol esters, and geranyl tiglate. (These tables are reproduced, by permission, in "The Chemistry of Essential Oils" (E. J. Parry), vol. ii., 4th ed., pp. 323-333, *q.v.*) The detection of artificial esters is the subject of a separate monograph (*q.v.*). Although most of the following artificially prepared esters and their corresponding alcohols are described separately elsewhere, the following summary of their odour characters by Prins and Schwarz (*P. & E. O. R.*, 1916, 335) may be usefully given here:—

Benzyl alcohol: Odour not very strong, slightly bitter; reminds of benzaldehyde.

Benzyl formate : Odour very strong, sweet, pungent ; reminds of cinnamic aldehyde.

Benzyl acetate : Odour strong, fruity jasmin odour ; rather pungent.

Benzyl propionate : Flower odour with a fruity freshness ; very useful for finer soaps.

Benzyl butyrate : Sweet fruity odour (apricot).

Benzyl valerianate : Flower odour ; reminds of the esters of phenyl-ethyl alcohol.

Phenyl-ethyl alcohol : Has the well-known sweet rose odour ; reminds of benzyl alcohol.

Phenyl-ethyl formate : Has the sweet pungent odour of the chrysanthemum type.

Phenyl-ethyl acetate : Rose odour of the red rose type ; very much in use.

Phenyl-ethyl propionate : A fine rose odour of the fruity type.

Phenyl-ethyl butyrate : A fine distinctive rose odour with a tinge of a leaf-like odour.

Phenyl-ethyl valerianate : Has a distinctive rose leaf odour.

Phenyl-propyl alcohol : As yet rather unknown and high in price ; the odour combines the rose type of phenyl-ethyl alcohol with the heavier hyacinth type of cinnamyl alcohol.

Phenyl-propyl formate : Has a characteristic formate odour of the heavy, sweet honey and cinnamon type.

Phenyl-propyl acetate : Reminds of geranyl acetate, but has a characteristic flower odour. The cinnamon odour is not present.

Phenyl-propyl propionate : Has a heavy and sweet fruity odour.

Phenyl-propyl butyrate : Reminds of benzyl butyrate, but the odour is not so pungent, though very characteristic.

Phenyl-propyl valerianate : Heavy odour, not very strong.

Cinnamyl alcohol : Has the well-known slight hyacinth odour ; reminds slightly of cinnamon.

Cinnamyl formate : Has a very sweet characteristic formate odour.

Cinnamyl acetate : Flower odour, sweet and without cinnamon odour.

Cinnamyl propionate : Odour of the fruity order.

Cinnamyl butyrate : Odour reminds of phenyl-ethyl butyrate, but heavier.

Cinnamyl valerianate : Very characteristic rose odour, of the tea rose type.

Geraniol : The well-known rose-geranium-like odour, not very sweet.

Geranyl formate : Rose leaf odour, as yet not extensively used.

Geranyl acetate : Flower odour of the rose type with a leaf odour, not characteristic ; it is the geraniol ester chiefly in use.

Geranyl propionate : Highly characteristic rose odour, fresh flower odour.

Geranyl butyrate : Sweet odour of the fruity type, reminds strongly of fresh apples (*reinettes d'or*).

Geranyl valerianate : Odour fruity, reminds of the acetate, not characteristic.

Citronellol : Has a distinct, sweet characteristic rose odour, much more pronounced than the odour of geraniol.

Citronellyl formate : A characteristic formate odour, sweet and more rose-like than geranyl formate.

Citronellyl acetate : Reminds very much of phenyl-ethyl acetate, fine rose odour.

Citronellyl propionate : Exceedingly sweet and lasting rose odour of the heavy and Oriental kind.

Citronellyl butyrate : Sweet rose odour, more flower-like and less fruity than geranyl butyrate.

Citronellyl valerianate : Rose-like odour, but not strong.

See also "Artificial Esters."

**ESTRAGOL.**—Estragol, or methyl chavicol,  $C_{10}H_{12}O$ , is the principal constituent of estragon or tarragon oil, and is also found in anise bark, bay and fennel oils. It is a highly odorous oil of specific gravity 0.972 ; refractive index, 1.5220 ; and boiling point, 216°. This body is responsible for the flavour of tarragon vinegar, in which the herb is used, as it is in wines of the Vermouth type. It is not used to any extent in perfumery proper.

**ESTRAGON OIL.**—Estragon or tarragon oil is an essential oil employed in the manufacture of wines, and in aromatic vinegars. It is distilled from the flowering herb *Artemisia Dracunculus*, the yield being from 0.25 to 0.8 per cent. on the dried plant. It is a colourless or pale yellowish-green oil, with an odour recalling that of aniseed, and having the following characters : specific gravity, 0.900 to 0.945 ; optical rotation,  $+2^{\circ}$  to  $+9^{\circ}$  ; refractive index, 1.5020 to 1.5140 ; acid value, 0 to 1 ; ester value, 1 to 9 ; and ester value after acetylation, about 15. *Roure-Bertrand Fils*, however, have found a sample, distilled by themselves, with the abnormal specific gravity 0.981. The oil contains much methyl-chavicol (estragol).

**ETHYL ACETATE.**—Magnolia oil contains a very small quantity of ethyl acetate  $\text{CH}_3\text{COO}\cdot\text{C}_2\text{H}_5$ . It has a very fruity odour, but is very soluble and very volatile, so that it does not play a very important part in perfumery. It boils at  $76^\circ$ . Its specific gravity is 0.906 to 0.907, and refractive index 1.373.

**ETHYL-AMYL-CARBINOL.**—This body is one of the isomeric octyl alcohols, of the formula  $\text{CH}_3(\text{CH}_2)_4\text{CH}(\text{OH})(\text{C}_2\text{H}_5)$ . It occurs naturally in oil of Japanese peppermint, and has been prepared artificially by Pickard and Kenyon (*Jour. Chem. Soc.*, 1913, 103, 1923) by passing the vapour of a mixture of 145 grams of normal caproic acid and 180 grams of propionic acid through a tube charged with thorium oxide at  $400^\circ$ . The ethyl-amylketone so obtained is reduced to the alcohol by moist ether and sodium.

The alcohol has also been synthesised by Schimmel & Co. (*Report*, April, 1912, 102; April, 1913, 82).

The following are the characters assigned to it by the chemists quoted :—

	Pickard and Kenyon.	Schimmel & Co.
Boiling point . . . .	$168^\circ\text{--}172^\circ$	$178.5^\circ\text{--}179^\circ$
Specific gravity . . . .	0.8247 at $\frac{20^\circ}{4^\circ}$	0.8276 at $15^\circ$
Optical rotation . . . .	+ $6.79^\circ$	+ $6.43^\circ$
Refractive index . . . .	1.4252	1.4275
Melting point of acid phthalate.	$66^\circ\text{--}68^\circ$	$65.5^\circ\text{--}66^\circ$
Melting point of semicarbazone.	$112^\circ$	$117^\circ$

**ETHYL-AMYL KETONE.**—This body,  $\text{C}_2\text{H}_5(\text{CO})(\text{CH}_2)_4\text{CH}_3$ , occurs naturally in French lavender oil. It is an aromatic oil, having a specific gravity 0.825; boiling point,  $170^\circ$ ; and refractive index, 1.4154. On oxidation it yields normal caproic acid. It forms a semi-carbazone melting at  $117^\circ$  to  $118^\circ$ .

**ETHYL ANISATE.**—This body is a crystalline body, of the formula  $\text{C}_6\text{H}_4(\text{OCH}_3)(\text{CO}_2\cdot\text{C}_2\text{H}_5)$ . It has a fine odour of chervil.

**ETHYL ANTHRANILATE.**—This ester,  $\text{C}_6\text{H}_4\cdot(\text{NH}_2)(\text{CO}_2\text{C}_2\text{H}_5)$  is a very odorous liquid boiling at  $260^\circ$ . It occurs in a few essential oils, and is of fine neroli odour. It closely resembles

methyl anthranilate (*q.v.*), but is rather sweeter and softer in perfume, and does not discolour so readily. It can be prepared artificially by the action of hydrochloric acid on ethyl alcohol and anthranil-carbonic acid (isatoic acid). It is useful in artificial neroli and jasmin.

**ETHYL BENZOATE.**—This ester,  $C_6H_5.COO.C_2H_5$ , is not a natural constituent of any essential oil, so far as at present known. It is used in the preparation of artificial ylang-ylang and similar flower oils, and is used generally for the same purposes as the corresponding methyl ester, which is known as niobe oil. It is prepared artificially by the condensation of ethyl alcohol and benzoic acid by means of hydrochloric acid. It is a sweet-smelling oil, which has the following characters: specific gravity, 1.0502 to 1.0530; refractive index, 1.5050 to 1.5063; and boiling point,  $212^\circ$ . It is soluble in 2 volumes of 70 per cent. alcohol and in 7.5 volumes of 60 per cent. alcohol.

**ETHYL BUTYRATE.**—Pineapple essences invariably contain this most useful fruit ester, a liquid boiling at  $121^\circ$ , of fine fruity odour. It has the formula  $CH_3(CH_2)_2COO.C_2H_5$ . It is useful in minute quantities for modifying artificial rose and similar odours. The commercial article consists of a mixture of isomers, with a boiling range from about  $115^\circ$  to  $140^\circ$ . It is never a very pure article.

**ETHYL CAPROATE.**—This ester (ethyl hexoate) is occasionally used for its fruity odour. It has a specific gravity 0.877; refractive index, 1.4075; and boils at  $167^\circ$ .

**ETHYL CAPRYLATE.**—Ethyl caprylate (ethyl octoate)  $CH_3(CH_2)_6COO.C_2H_5$  is an ester having an odour recalling that of secondary products of vinous fermentation. It is probably a constituent of oil of cognac, and is useful in modifying floral bouquets. Its specific gravity is 0.873; refractive index, 1.4171; and boiling point,  $208^\circ$ .

**ETHYL CINNAMATE.**—The cinnamic ester of ethyl alcohol  $C_6H_5.CH:CH.COOC_2H_5$  is not often found naturally, but is a constituent of the essential oils of *Kaempferia galanga* and *Storax*. It is prepared artificially by passing a current of dry hydrochloric acid gas through an alcoholic solution of cinnamic acid. It is an odorous liquid, optically inactive, solidifying on cooling, and melting at  $12^\circ$ . It has a specific gravity 1.050 at  $20^\circ$



refractive index, 1.5590 ; and boiling point, 271°. It is useful in sweet, heavy bouquets of the Oriental type, and also in eau de Cologne where a heavy, persistent sweet tone is desired.

**ETHYL CITRATE.**—See “Esters, Artificial.”

**ETHYL-DECINE-CARBONATE.**—This new synthetic is analogous to the corresponding heptene-carbonate. Its formula is  $C_8H_{17}C : C.COOC_2H_5$ . It is an oil having a “leafy” perfume, recalling that of mignonette, in which type of perfume it is of considerable value.

**ETHYL DECYLATE.**—The ethyl ester of capric, or decylic, acid,  $CH_3(CH_2)_8CO_2C_2H_5$  is a synthetic perfume, prepared by the esterification of capric acid, which is present in cocoa nut oil, with ethyl alcohol. It has a floral odour and is useful in artificial rose perfumes.

**ETHYL FORMATE.**—This ester resembles ethyl acetate in general characters, but has a rather sharper odour. It is a liquid of specific gravity, 0.926 ; refractive index, 1.3600 ; and boiling point, 55°.

**ETHYL-HEPTENE-CARBONATE.**—This expensive substance,  $C_8H_{17}C : C.COOC_2H_5$ , is one of the most recent synthetic perfumes, having what is known as a “green leaf” effect, especially in the modification of the pure *flower* effects in violet and rose perfumes. (*Vide* Amyl-heptene-carbonate.)

**ETHYL HEPTOATE.**—Oenanthylic ether is the common name for this ester. It has a fragrant odour recalling that of the secondary constituents of vinous fermentation. It is sold in a nearly pure condition as artificial oil of cognac. It is an oil boiling at 188°, and is used to a limited extent in the manufacture of artificial flavouring essences, and in artificial flower extracts. Its specific gravity is 0.871, and refractive index 1.4140.

**ETHYLISOAMYL-OXY-BUTYRATE.**—This ester, recently synthesised by Bogert and Slocum (*American Perfumer*, xviii., 12, 621), possesses a fine fruity odour. The free acid when distilled under reduced pressure gives isoamylbutyrolactone, an oil boiling at 131° to 134° at 12 mm., having a fine odour of peaches.

**ETHYL LAURINATE.**—This ester is used in very small quantities in the preparation of artificial flower perfumes, such as

mignonette and tuberose. It is an oil of very sweet, fruity odour, and of intense strength. It boils at  $269^{\circ}$ , and has the formula  $\text{CH}_3(\text{CH}_2)_{10}\text{COOC}_2\text{H}_5$ .

**ETHYL MALONATE.**—Malonic ether, as the diethyl ester of malonic acid is usually termed, is of great value in general synthetic chemistry, but has also recently been recognised as a useful artificial perfume. Its odour is fruity, recalling that of apples, but much sweeter than that of the valerianic ester. It is prepared by treating either potassium cyanacetate or malonic acid with ethyl alcohol and hydrochloric acid. It is an oil of specific gravity 1.070, and boiling at  $198^{\circ}$ . Its formula is  $\text{CH}_2(\text{COOC}_2\text{H}_5)_2$ .

**ETHYL MYRISTINATE.**—This ester is a semi-solid body, melting at  $11^{\circ}$  and boiling at  $295^{\circ}$ . Its formula is  $\text{CH}_3(\text{CH}_2)_{12}\text{COOC}_2\text{H}_5$ , and it is prepared by the esterification of myristic acid and ethyl alcohol by means of hydrochloric acid. It is of powerful and persistent odour, and is useful both as a fixative and in modifying floral odours, especially violet perfumes.

**ETHYL-OCTINE-CARBONATE.**—This is still an experimental synthetic. It is analagous in all respects to the corresponding heptene-carbonate. Its formula is  $\text{C}_6\text{H}_{13} \cdot \text{C} : \text{C} \cdot \text{COOC}_2\text{H}_5$ .

**ETHYL OLEATE.**—Ethyl oleate is an ester principally used as an "artificial" ester for adulteration purposes. (*Vide* "Esters, Artificial.") It has, however, a slight floral odour, and also fixative properties. It is a liquid of the formula  $\text{C}_{17}\text{H}_{33} \cdot \text{COO} \cdot \text{C}_2\text{H}_5$ , boiling at about  $340^{\circ}$ .

**ETHYL PELARGONATE.**—This ester (ethyl nonylate), of the formula  $\text{CH}_3(\text{CH}_2)_7\text{COOC}_2\text{H}_5$ , is a very fragrant oil made by melting undecylenic acid with caustic potash, and setting free the resulting pelargonic acid by dilute sulphuric acid. This acid is then esterified with ethyl alcohol in the presence of sulphuric acid, and purified by fractional distillation. It boils at  $100^{\circ}$  to  $110^{\circ}$  at 10 mm. pressure, or at  $228^{\circ}$  at normal pressure. It has a specific gravity 0.876, and refractive index 1.4255.

**ETHYL-PHENYLACETATE.**—This ester is formed by the condensation of ethyl alcohol and phenyl-acetic acid. It is a very sweet smelling oil with an odour recalling honey and roses. It is very useful in compounding artificial rose odours. Its formula is  $\text{C}_6\text{H}_5 \cdot \text{CH}_2 \cdot \text{COOC}_2\text{H}_5$ . It has a specific gravity about 1.0366; refractive index, 1.4990;  $n_D^{20}$  boils at  $127^{\circ}$ .

**ETHYL PHTHALATE.**—As a perfume ethyl phthalate has no value. It is, however, of considerable service as a solvent for artificial musk, and has also a fixative value. Its principal use, however, is as an “artificial” ester for the purposes of adulteration. It is a liquid of specific gravity, 1.124; refractive index, 1.5020; and boils at 293°. One per cent. indicates, in the usual method of analysis, 1.77 per cent. of linalyl acetate. Its formula is  $C_6H_4(COOC_2H_5)_2$ . It is prepared by the esterification of phthalic acid with ethyl alcohol.

**ETHYL SALICYLATE.**—The usual artificial wintergreen oil is methyl salicylate (*q.v.*). The ethyl ester,  $C_6H_5.CH_2.COOC_2H_5$  is a liquid boiling at 234°; of specific gravity, 1.1372; refractive index, 1.5234; and optically inactive. It solidifies at low temperatures, and melts at 1.3°. It is an oil having a very fine wintergreen odour, more delicate than that of the methyl ester.

**ETHYL SUCCINATE.**—Succinic ether has no legitimate use in perfumery, but is used as an “artificial” ester for adulteration purposes. It is an oil boiling at 216°, and has a specific gravity 1.044. One per cent. appears in the usual method of analysis as 2.26 per cent. of linalyl acetate. It results from the esterification of succinic acid and ethyl alcohol.

**ETHYL VALERIANATE.**—This ester,  $C_4H_9.COOC_2H_5$  is an oil with a powerful fruity odour. It results from the esterification of valerianic acid and ethyl alcohol. The commercial article is a mixture of isomers, of specific gravity about 0.875; refractive index, 1.3980; and boiling point, 135°.

**EUCALYPTOL.**—This body, or cineol as it is more scientifically termed, is the characteristic constituent of the majority of the eucalyptus oils. There are, of course, a certain number of the oils of this species which are free, or practically free, from this constituent. The eucalyptus oils which contain eucalyptol are used to some extent in perfumery, but rather as antiseptics than as pleasant odour bearers. Eucalyptol is an oxide, of the formula  $C_{10}H_{18}O$ , having a specific gravity 0.930; refractive index, 1.4590; melting point, +1°; and boiling point, 176° to 177°. The usual process for the determination of eucalyptol in eucalyptus and other oils containing eucalyptol is that devised by Scammel. This, as used to-day, is carried out as follows. To a known weight (about 5 grams) of the oil, from 1 to 1.5 times its weight of phosphoric acid, of specific gravity 1.75, is slowly added, drop by

drop, with continual stirring, the mixture being kept cold all the time. The crystalline magma which results is strongly pressed between filter paper after as much as possible of the terpenes present has been drained off. The crystalline mass is, after repeated pressing, decomposed by hot water in a flask with a graduated neck, and the liberated eucalyptol measured off in the neck. There are several other methods of determination of eucalyptol, but the only one possessing any merits comparable with those of the original phosphoric acid method is that devised by Cocking (*P. & E. O. R.*, 1920, 281), and varied by Walker. This method is a physical one, and depends on the determination of the freezing point of a mixture of the oil containing eucalyptol and *ortho*-cresol in proportions corresponding approximately with the molecular weights of the two substances. A stout-walled tube suspended by a wire loop to the balance is used for the determination. Into this is weighed 3 grams of the oil and 2.1 grams of melted *ortho*-cresol. The tube is then removed from the balance and inserted through a bored cork into a wide-mouthed bottle containing water, which can be heated or cooled as necessary. The mixture is agitated, and the solidifying point noted. It is then warmed until melted, and the solidifying point again noted. This process is repeated until the solidifying point becomes constant. With a pure *ortho*-cresol melting at 30° the following results were obtained with mixtures of known eucalyptol content:—

Per cent. of eucalyptol.	Freezing points (varying according to the nature of the admixture).
100 . . . . .	55.2°
95 . . . . .	53.4°–53.6°
90 . . . . .	51.2°–51.7°
85 . . . . .	48.5°–49.7°
80 . . . . .	45.8°–47.7°
75 . . . . .	43.2°–45.7°
70 . . . . .	40.6°–43.8°
65 . . . . .	37.4°–41.2°
60 . . . . .	34.2°–37.4°
55 . . . . .	29° –33.6°
50 . . . . .	25.4°–29.8°
45 . . . . .	22.2°–26.2°

Walker (*Jour. Soc. Chem. Ind.*, December, 1923) prefers the use of *a*-naphthol to *o*-cresol in the freezing point determination, on account of the non-hygroscopic nature of the compound. This modification has been criticised by Cocking (*P. & E. O. R.*, 1924, 10), who states that:—

"(1) In the cresineol method the freezing point is the temperature at which the solid cresineol separates from the mother liquor, which latter consists of a saturated solution of cresineol in a mixture of the non-cineol portion of the oil, and *o*-cresol in *unvarying proportions*.

"*This mixture is permanently liquid at the temperature of the test.*

"(2) In Walker's proposed modification the freezing point is influenced by the crystallising out of the  $\alpha$ -naphthol in addition to the  $\alpha$ -naphthol-cineol compound, and thus the mother liquor will consist of the non-cineol portion of the oil saturated with  $\alpha$ -naphthol and with the  $\alpha$ -naphthol-cineol compound, the relative proportions of which will vary with the temperature. It is thus apparent that, while this modified method may give fairly accurate results on oils containing from 100 to 50 per cent. of cineol, it cannot be relied upon, as the freezing points obtained with such oils are also given by oils containing from 0 to 50 per cent. of cineol."

For other methods of determining eucalyptol, see "The Chemistry of Essential Oils, etc." (E. J. Parry), vol. ii., 4th ed., p. 276.

**EUCALYPTUS CITRIODORA.**—This tree is known as the citron-scented eucalyptus, and is found along the coast of Queensland and as far south as Port Jackson. It has been stated to be a variety of the New South Wales spotted gum, *Eucalyptus maculata*, but it is considered by Baker and Smith to be a separate species. The essential oil is well known, having been on the market for some years. As the tree is a tall one, the cost of collecting the material for distillation is high, and as the yield is only about 0.75 per cent., the cost of the oil is at present rather out of proportion to its perfume value as compared with other oils of the same type of odour. It is so rich in citronellal that it is undoubtedly the best source (apart from questions of price) of that body, and citronellol produced therefrom is said to be superior to that from any other source except *Leptospermum citratum*. And since it is possible, by fractional distillation only, to raise the aldehydes to 98 per cent., they can be reduced directly, without the expense of previous separation by means of their bisulphite compounds. The tree has been extensively cultivated in private gardens in and around Sydney for ornamental purposes. In its native state it has never been found further south than Bundaberg, in Queensland. The oils from the wild

and the cultivated trees have given the following results on distillation :—

	Wild.	Cultivated.
Specific gravity . . .	0.864–0.905	0.861–0.866
Optical rotation . . .	– 1° to + 2°	0° to – 1.15°
Refractive index . . .	1.4540–1.4678	1.4498–1.4515
Citronellal . . .	Up to 95 per cent.	95–98 per cent.

It also contains traces of geraniol and pinene. It is far more delicate in odour than any type of citronella oil. The tree much improves by cutting, and if cultivated as a small tree the leaves can be collected at a cheap rate. Many cultivated trees have been found to yield well over 1 per cent., even up to 1.5 per cent., of oil, which is a great increase over that obtained from the wild trees. The small trees can be cut when they are from three to five years old. The cultivation of this tree on a commercial scale would probably be exceedingly remunerative, and allow the oil to compete successfully with Java and Burmese citronella oils. (*Vide Bulletin No. 5, Technological Museum, Sydney, N.S.W., 1923.*)

**EUCALYPTUS MACARTHURI, OIL OF.**—Amongst the perfume-bearing oils recently examined, and which are derived from raw material grown in the British Empire, that of *Eucalyptus Macarthuri* is one of the most remarkable, and is worthy of very considerable attention. The oil is at present almost entirely consumed locally in Australia as a denaturant of alcohol for perfumery purposes. It is an oil which is extraordinarily rich in geranyl acetate, so much so that, by skilful manipulation, geranyl acetate of 80 to 85 per cent. strength, the balance being principally free geraniol, can be produced from it without acetylation. As the species is somewhat sparsely distributed, attempts have been made to cultivate it in Australia, and, being one of the apparently stable species, the oil seems to remain constant in composition. There is a plantation at Emerald, in Victoria, started in 1911, which has given good results. A sample of the oil distilled by Penfold (*Bulletin No. 5, Technological Museum, Sydney, N.S.W., 1923*) from leaves of plants grown at Croydon, near Sydney, from seeds collected by Dr. Guthrie, gave the following results on analysis : yield of oil, 0.26 per cent. ; specific

gravity at 15°, 0.9274; optical rotation, + 3.1°; refractive index, 1.4744; and geranyl acetate, 67 per cent. Trees grown at Longueville and Ashfield from seedlings taken from Croydon gave essential oils which yielded the following results on analysis:—

	Longueville.	Ashfield.
Yield of oil per cent. . . . .	0.2 ..	0.74
Specific gravity . . . . .	0.9255 ..	0.9257
Optical rotation . . . . .	+ 3.2° ..	+ 3.5°
Refractive index . . . . .	1.4692 ..	1.4696
Esters as geranyl acetate	74.8 per cent.	70.2 per cent.
Free geraniol . . . . .	7.1 „ ..	6 „
Eudesmol . . . . .	16.5 „ ..	16.1 „

The trees can be cut for distillation every year and yet produce their full quantity of leaf for next year's cutting. By keeping them as small trees they yield more foliage, and the cost of collection is less. Moisture is essential, but the tree will grow in poor soil, although a good soil will cause an increased yield of oil. The oil has been recommended as a source of geraniol, though, as this requires a preliminary saponification, it is probable that the cost would be prohibitive; but as a source of geranyl acetate the tree would probably amply repay careful cultivation.

**EUCALYPTUS PIPERITA.**—This species of eucalyptus may be of considerable commercial importance as a source of supply for piperitone, if this substance should, as hoped, prove a suitable raw material for the manufacture of thymol or menthol.

It is ("A Research on the Eucalyptus," Baker and Smith, 2nd ed., 274) a tall tree with a fibrous bark, found round Sydney and in Victoria and Queensland. The account of the yield and characters of the essential oil distilled from the leaves and terminal branchlets in 1897 given by Baker and Smith (*loc. cit.*) has quite recently been supplemented by Penfold and Morrison (*Jour. and Proc. Roy. Soc. N.S.W.*, lviii., 1924, 124).

It is pointed out that Baker and Smith gave the yield of oil as 0.8 per cent., the oil, on distillation, yielding 85 to 86 per cent. distilling below 200°. Although there is no record of the quantity of piperitone present in this species, it could not have been more than 5 to 10 per cent., and this has usually been assumed to be the case. Many inquiries have been made by persons clearing their property of this species for information regarding the oil, and they were advised according to the foregoing results. Field observations made by Penfold and Morrison during the past few years, however, led them to suspect that the trees of this

species growing around Port Jackson contained much more than the published yield of oil (0·8 per cent.), and, from the odour of the crushed leaves, that piperitone was present in considerable quantity. Consequently, they decided to reinvestigate the matter, and material was collected from such places as Longueville, Kuringai, Como, etc., with the result that field observations were confirmed. The leaves and terminal branchlets, cut as for commercial distillation, collected about the same period of the year, March–April, and weighed when fresh, yielded from 2 to 2·5 per cent. of oil, containing 40 to 50 per cent. of piperitone. The oils thus obtained closely resembled those from *E. dives*, so much so that it is doubtful if an unlabelled specimen of each could be differentiated. These results are especially interesting, as they confirm in a very striking manner the observation of Surgeon-General White made in the “Journal of a Voyage to New South Wales,” published in London in 1790, that the name of “Peppermint Tree” had been given to this plant on account of the very great resemblance between its essential oil and that of the English peppermint, *Mentha piperita*. Such a description would appear most unlikely if the oil had resembled that described by Messrs. Baker and Smith, where the piperitone content did not exceed 10 per cent. These authors state, in the work mentioned, page 274, under Remarks: “In this research particular interest pertains to this species, as it was from trees of the ‘Sydney Peppermint,’ growing where Sydney now stands, that the first eucalyptus oil was obtained. It was distilled by Dr. White, Surgeon to the First Fleet, in 1788, and it seems remarkable that they did not, at the time of their investigation, examine the oils from trees growing in or around Sydney as well as those from fifty to 100 miles away. It is probable that the composition of the oil, described below, closely resembles that first distilled in 1788.”

In view of the disparity between Baker and Smith’s results and those now recorded, Penfold and Morrison have carried out a considerable number of observations and experiments on oils obtained from this species growing in various localities and altitudes, and have come to the conclusion that, apart from slight variations likely to be due to the influence of ecological conditions, there are two very distinct forms of this tree, one growing close around Sydney—say, the Port Jackson district—yielding 2 to 2½ per cent. of oil containing 40 to 50 per cent. of piperitone, and the other yielding only 0·6 to 0·8 per cent. of oil low in piperitone, but high in phellandrene and eudesmol, and containing



up to 20 per cent. of cineol, found principally in the more mountainous districts. This latter is tentatively termed the mountain form, or variety "A," to distinguish it from the typical form.

The type *E. piperita* and its varied forms are being carefully studied, and the final result of their observations will be dealt with in a later publication. Meanwhile, they prefer merely to direct attention to the striking difference in the composition of the oils of two very distinct forms, and to the interesting nature of that obtained from trees growing at Port Jackson, the chemical and physical constants of which are totally different to anything that has previously been published concerning the oil of this species.

In the table particulars are given only of the oils from the Port Jackson trees, those from other localities being left for a later communication.

The oils distilled by Penfold and Morrison had the following characters :—

Date.	Locality.	Weight of Leaves. Lbs.	Yield of Oil. Per cent.	Specific Gravity $\frac{15}{15}^{\circ}$ .
18/3/1924	Longueville .	161	2.01	0.8924
29/3/1924	Kuringai .	104	2.42	0.9016
8/4/1924	Como .	28	2.02	0.8977

Optical Rotation.	Refractive Index, 20°.	Solubility in 70 per cent. Alcohol. Vols.	Piperitone Content. Per cent.
— 64.60°	1.4805	1 in 9	42
— 52.00°	1.4821	1 in 5.6	42
— 62.75°	1.4805	1 in 5.3	48

These oils on distillation yielded, on an average, 40 per cent. distilling at 60° to 75° at 10 mm., 18 per cent. at 75° to 100°, and 42 per cent. at 100° to 110°.

*Separation of Phellandrene and Piperitone.*—The portion distilling at 60° to 75° at 10 mm., on fractionation, readily yielded phellandrene of boiling point 59° to 61° at 10 mm., having a specific gravity at 15°/15° of 0.8467; optical rotation, — 93°; and refractive index, 20°, 1.4729. The last fraction (boiling point, 100° to 110° at 10 mm.) was found to consist principally of levorotatory piperitone having an optical rotation of — 57°. On purification through the bisulphite compound, it possessed the following characters: boiling point at 10 mm., 107° to 108°; specific gravity, 15°/15°, 0.9386; optical rotation, — 10°; and

refractive index, 20°, 1.4836. Cineol was not detected in the terpene fraction.

The oil described by Baker and Smith had the following characters :—

Specific gravity . . . . .	0.911
Optical rotation . . . . .	— 2.7°
Refractive index . . . . .	1.4781
Saponification value . . . . .	11

**EUCALYPTUS STAIGERIANA.**—This tree is known as the lemon-scented ironbark of Queensland. It is a medium-sized tree, and so far has only been found in the Palmer River district of north Queensland.

The oil was referred to by *Schimmel & Co.* as far back as 1888 (*Semi-Annual Report*). According to Baker and Smith, the dried material yielded from 2.5 to 3 per cent. of oil having a specific gravity 0.8715; optical rotation, — 38°; refractive index, 1.4814; and containing 60 per cent. of *lævo*-limonene, 16 per cent. of citral, the remainder being geraniol, geranyl acetate, and a sesquiterpene. Two samples recently examined by Penfold (*Bulletin No. 5, Technological Museum, Sydney, N.S.W., 1923*) gave the following results :—

	1.	2.
Percentage yield . . . . .	2.59 per cent.	—
Specific gravity . . . . .	0.8777 ..	0.8822
Optical rotation . . . . .	— 34.6° ..	— 26.4°
Refractive index . . . . .	1.4793 ..	1.4797
Citral . . . . .	28 per cent.	38 per cent.

This oil has been said by experts to be suitable for flavouring confectionery in the place of lemon oil, and also to be suitable for denaturing alcohol to be used for the manufacture of eau de Cologne.

**EUCALYPTUS STUARTIANA.**—The eucalyptus oil from this tree has an odour recalling that of apples. It contains eucalyptol, pinene, and esters which have not been fully investigated. It has a specific gravity 0.916; optical rotation, + 4.7°; and refractive index, 1.4780.

**EUDESMOL.**—This compound is a crystalline body, melting at 80°, of the formula  $C_{15}H_{26}O$ , which is a sesquiterpene alcohol. It was first isolated from the oil of *Eucalyptus piperita* by H. G. Smith (*Jour. Proc. Roy. Soc. N.S.W., 1899, 33, 86*), and later examined by Semmler and Mayer (*Berichte, 1912, 45, 1390*), and Semmler and Tobias (*Berichte, 1913, 46, 2026*). It is a crystalline

body melting at 78°, boiling at 156° at 10 mm., of specific gravity 0.9884 at 20°, and refractive index 1.5160.

**EUGENIA APICULATA, OIL OF.**—The Chilian plant *Eugenia apiculata* possesses leaves which are used to a considerable extent as a drug. According to *Schimmel & Co. (Report, October, 1910, 145)*, it yields 1.27 per cent. of essential oil having an odour recalling that of myrtle. Its characters are as follows :—

Specific gravity . . . . .	0.892
Optical rotation . . . . .	+ 12° 40'
Refractive index . . . . .	1.4782
Acid value . . . . .	5.5
Ester value . . . . .	25.8
Ester value after acetylation . . . . .	65.3

**EUGENIA CHEKEN, OIL OF**—The leaves of *Eugenia cheken*, a plant belonging to the natural order *Myrtaceæ*, indigenous to Chili, yield about 1 per cent. of an essential oil having a pleasant odour recalling those of sage and eucalyptus. It is of a yellowish-green colour, and has the following characters :—

Specific gravity . . . . .	0.8795
Optical rotation . . . . .	+ 23.5°

The only constituents so far identified are pinene and cineol.

**EUGENIA JAMBOLANA.**—The seeds of this plant, a member of the natural order *Myrtaceæ* and a native of the West Indies, are known as jambul seeds. Power and Callan (*Pharm. Jour.*, 1912, 88, 414) have distilled the essential oil, which is pale yellow in colour and very aromatic. It has a specific gravity 0.9258 at  $\frac{20^\circ}{20^\circ}$ , and an optical rotation — 5° 42'.

**EUGENIA OCCLUSA, OIL OF.**—*Schimmel & Co. (Report, April, 1911, 123)* have reported on an oil known in Java as “salam oil.” It is distilled from the leaves of *Eugenia occlusa*, the yield being about 0.05 per cent. Its properties are as follows :—

Specific gravity . . . . .	0.9567
Optical rotation . . . . .	— 1° 40'
Refractive index . . . . .	1.4681

It contains citral and other aldehydes not yet identified.

**EUGENIA UNIFLORA, OIL OF.**—According to Peckolt (*Berichte d. Deutsch. Pharm. Ges.*, 1903, 13, 130), the seeds of *Eugenia uniflora* yield about 0.043 per cent. of a yellowish essential oil having an aromatic pepper-like odour. The leaves yield about 0.14 per cent. of a similar oil, of specific gravity 0.963.

**EUGENOL.**—Eugenol,  $C_{10}H_{12}O_2$ , is a phenol occurring in oils of clove, cinnamon leaf, bay, pimento, and others. It is the characteristic odour bearer of clove oil, in which it occurs to the extent of from 80 to 95 per cent. It is used to a very considerable extent as the raw material for the manufacture of vanillin, and to a small extent for the manufacture of isoeugenol. Both eugenol and isoeugenol are necessary constituents of all carnation perfumes (*q.v.*).

Eugenol is a pale yellowish oil of intense clove odour, having a specific gravity 1.070; refractive index, 1.5439; and boiling point,  $252^{\circ}$  to  $254^{\circ}$ . It forms a characteristic benzoyl derivative melting at  $69^{\circ}$  to  $70^{\circ}$ , and a diphenylurethane melting at  $107^{\circ}$  to  $108^{\circ}$ .

Eugenol in essential oils is almost invariably determined by absorption by means of a solution of caustic soda (*vide* "Phenols, Determination of"). A more elaborate method, which possibly gives more accurate results, is that devised by Thoms, which is as follows. About 5 grams of the oil are weighed into a small beaker and 20 grams of a 15 per cent. solution of caustic soda added, and then 6 grams of benzoyl chloride. The mixture is well stirred, and the whole eventually sets to a solid mass, much heat being evolved. To this mass 50 c.c. of water are added and the mixture warmed on a water bath until the compound is completely melted, the mixture well stirred, and allowed to cool again. The clear supernatant aqueous liquid is filtered off and the crystalline mass twice remelted and washed with 50 c.c. of water. The crude benzoyl-eugenol is then recrystallised from 25 c.c. of hot alcohol, which is first passed through the filter in order to dissolve any benzoyl-eugenol thereon. The liquid is cooled to  $17^{\circ}$  and the crystalline precipitate collected on a small weighed filter paper, filtered, and washed with 90 per cent. alcohol, until the filtrate measures exactly 25 c.c. The filter paper and crystals are weighed after being dried to constant weight at  $100^{\circ}$  C. To the weight so obtained 0.55 gram is added to allow for the solubility of the benzoyl-eugenol in the 25 c.c. of 90 per cent. alcohol. From this the weight of eugenol is calculated, the molecular weight of eugenol being 164, and that of benzoyl-eugenol 268. This method is not used, however, for commercial analysis.

**EUPATORIUM, OILS OF.**—*Eupatorium fœniculaceum* is a herb known as dog fennel, and is distributed through the northern parts of America. It yields on distillation an essential oil of a golden yellow colour and a pepper-like odour. Miller

(*Bull. Univ. of Wisconsin*, 1914, 693, 7) has examined a number of samples distilled in Alabama, the yield of oil being about 1 per cent. The principal constituent of the oil is the dimethyl ether of thymohydroquinone. Bornyl acetate, borneol, linalol, phellandrene, and probably sabinene, are present in the oil. It has a specific gravity 0.919 to 0.960; refractive index, 1.497 to 1.507; optical rotation,  $-16.7^{\circ}$  to  $+14.3^{\circ}$ ; and contains from 46 to 66 per cent. of thymohydroquinone dimethyl ether. The oil distilled from *Eupatorium triplinerve*, a plant indigenous to tropical America and found wild in other tropical countries, is of similar composition.

**EURYANGIUM SUMBUL.**—This plant, also known as *Ferula Sumbul*, possesses a highly odorous root, known as sumbul root. On distillation it yields 0.2 to 1.7 per cent. of a viscid dark-coloured oil having a musk-like odour. Its specific gravity is 0.941 to 0.964; optical rotation about  $-6^{\circ}$ ; acid value, 7; and ester value, 17 to 85. Its constituents have not yet been investigated.

**EURYBIA AROPHYLLA.**—This tree is one of the natural order *Compositæ*, and is confined to Australia, Tasmania, and New Zealand. Its leaves have a very pronounced odour of musk; hence its popular name the “silver-leaved musk tree.”

**EVERNIA PERFUMES.**—The extracts of *mousse de chêne* of commerce (*q.v.*) are obtained *inter alia* from *Evernia furfuracea* and *Evernia prunastri*, lichens flourishing on oak and other trees.

**EVODIA OILS.**—The evodia trees belong to a genus of small rutaceous trees or shrubs, mostly natives of tropical New Holland and the Indian archipelago. Most of the species are very sweet-scented plants. The best known are *Evodia Hortensis*, a native of the Friendly Islands and the New Hebrides, a plant whose leaves are used by the natives to perfume coconut oil; *Evodia simplex*, and *Evodia Rutaecarpa*. The oil distilled from *Evodia simplex* in Réunion was found by Schimmel & Co. (*Bericht*, October, 1906, 83) to have the following characters:—

Specific gravity at $15^{\circ}$	0.8737
Optical rotation	$-13^{\circ} 4'$
Acid value	2.1
Ester value	16.4
Ester value after acetylation	63.3

The oil contains methyl-eugenol and a crystalline hydrocarbon melting at  $81^{\circ}$ .

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The essential oil distilled from the fruit of *Evodia Rutaecarpa* has been examined by Asahina and Kashiwaki (*Jour. Pharm. Soc. Japan*, November, 1915). These chemists isolated from it a terpene which they termed evodene, which is allied to the olefinic terpenes of which myrcene is a type.

**EXCÆCARIA AGALLOCHA.**—This plant, which belongs to the natural order *Euphorbiaceæ* is a highly odorous tree, the wood being used in Dutch East Indies as a fumigant under the name *Menengen*. The heart-wood of young trees is the most odorous, the wood of old trees becoming almost odourless as resinification takes place. The constituents have not been fully investigated, but an alcohol melting at 85° is present in the form of an ester.

**EXOTHEA COPALILLO.**—An oil distilled in Mexico from this tree known as copalillo oil has been examined by *Roure-Bertrand Fils* (*Bulletin*, 1914–1919, 138). It is a dark yellow oil with an odour recalling that of linaloe oil. It had the following characters :—

Specific gravity	.	.	.	.	0.8504
Optical rotation	.	.	.	.	+ 0° 50'
Acid value	.	.	.	.	10.2
Ester value	.	.	.	.	13.1

**EXTRACTION OF PERFUMES FROM PLANTS.**—The methods used for the extraction of the perfume material from the plant are extremely variable. The methods themselves are, in general, old-established in principle, but during the last few decades scientific investigation has been brought to bear upon the questions involved, and there has been a vast improvement in the methods in which these processes have been applied. Fifty years ago, distillation, for example, was just distillation, and that was all. The effects of time, pressure, and temperature were practically neglected; esters were hardly known, and if they were decomposed during the process of distillation, so much the worse for the resulting oil. To-day, knowledge of the characters of the constituents of essential oils, and of the conditions under which they are extracted in the most perfect condition, has advanced to such an extent that many raw materials for perfumery are undoubtedly prepared in an ideal manner. At the same time, one has to remember that many of the plants used for the extraction of perfumes grow wild, or are cultivated in spots far distant from large towns and under such conditions that

the time occupied in transporting the raw material to an up-to-date factory in a large town would, if such transport were possible, cause the material to deteriorate to such an extent that the resulting perfume would be largely spoiled. The most scientific factories and apparatus can only exist economically where there is within reasonable distance a plentiful supply of the raw material to be treated. The majority of the natural perfumery materials which are employed to-day are the result of distillation processes. This method of production is dealt with under "Distillation" (*q.v.*).

For the preparation of a certain number of essential oils, however, distillation is not a suitable process, the oil being sufficiently altered by the exposure to heat and moisture to become of quite inferior quality. These oils are prepared by a cold process of expression. Still, other essential oils are of such a delicate character, and are present in such minute amounts, that no process of distillation or expression is practicable. For this type of oil, no separation is, in effect, possible on a commercial scale. The perfume is extracted by means of a solvent and marketed in admixture with other substances extracted at the same time, as, for example, in the form of absolutes, concretes, or pomades. For practical purposes, then, the methods of separation of the perfume materials from the plant may, apart from the collection of exudations, such as in the case of oleoresins, etc., be grouped in the above manner, namely, by (1) distillation, (2) expression, (3) extraction by solvents. Of these, as mentioned above, distillation is treated under its own heading.

The typical expressed oils of interest to the perfumer are those of lemon, bergamot, orange, and lime.

The bulk of the lemon oil of commerce is produced in Sicily, where it is prepared, practically entirely, by either the *Scorzetta* or the *Spugna* methods. Almost every other process which has from time to time been introduced has been discarded, and the older processes have not been improved upon. In the *Scorzetta* process, the fruits (lemons and oranges) are cut into halves by a sharp knife, either longitudinally or across. If the peel after the expression of the oil is destined for candied peel, it is usual to cut the fruits longitudinally. The pulp and juice are removed as completely as possible. The peel is soaked in water for several hours, which causes the cell walls to become stiffer and enables them to be more completely ruptured than would otherwise be the case, so that the oil globules are more completely discharged.

The men who actually express the oil sit in front of an earthenware jar, across which rests a bamboo stick, which supports several sponges, one of which is cup-shaped. The operator presses the peel into the sponge with one hand, the other hand pressing the sponge. This is done several times, the peel being turned round, so that as much as possible of the oil exuding from the burst oil cells is absorbed by the sponge. Where the peel has been cut longitudinally, round sponges are used in place of cup-shaped ones. The oil gradually collects in the jar, mixed with water, pulp, etc. The water is allowed to separate, and the oil is stored in a cold cellar, filtered, and stored in coppers or tins. The so-called *Spugna* method differs only from the above described in details. The peel is removed by three longitudinal incisions, the inside of the fruit remaining intact for after-treatment for the lemon juice. It is quite obvious that an essential oil prepared in this, or in similar manner, is not quite accurately described as an essential oil. It is really an essential oil holding in solution such dissolved substances as are present in the peel, and which have become dissolved in the oil. Hence, all such oils contain a fixed non-volatile residue when evaporated on the water bath, consisting of such solid or semi-solid dissolved substances.

The so-called *Ecuelle* method was formerly used in Nice and the neighbourhood, but is hardly ever employed to-day, except in the West Indies for the production of hand-pressed oil of limes. The process consists in causing the fruits to be rolled about in cup-shaped vessels the bottom and sides of which are covered with metal (brass, as a rule) needles. The oil cells are punctured, and the oil, with some watery liquid, gradually collects in a tubular extension of the vessel, and is collected and filtered as usual. The "Machine" process is practically confined to the expression of the oil from bergamot fruits. The most general mechanical appliance used is a primitive hand-worked machine, in which the round fruits are rotated between discs provided with either needle points or knives, suitable arrangements being made for the collection of the oil which exudes from the ruptured cells. It is obvious that in most of these somewhat crude processes, there must be a good deal of more or less waste residues. These are often worked up by distillation, so as to reduce the loss of oil to a minimum. The distilled oils, however, as has been indicated above, are of considerably inferior quality to the expressed oils, and are practically never marketed as such. They are usually kept separately and used to mix with the cheaper



qualities of the expressed oil. In dealing with these expressed oils, it must be remembered that not only must the water be completely removed from the oil (which is, of course, equally true for distilled oils), but also the albuminous and similar matter derived from the fruits, and which never occurs in distilled oils, must be got rid of completely, since such impurities tend to decompose, and impart a very unpleasant odour and flavour to the oil. (Refer also to U.S.A. Patent Specification No. 1353169; and *P. & E. O. R.*, 1921, 18.)

The solvent extraction processes may be divided into two principal classes. Of these the older is the extraction by means of a non-volatile solvent, such as animal fats or vegetable fixed oils. This method may be subdivided into (a) enfleurage, where only normal temperatures are employed, and (b) maceration, where heat is applied. The more recent process of extraction is that by means of volatile solvents, such as petroleum ether, where the solvent is driven off and the extracted perfume material, etc., is recovered and marketed in a concentrated form.

The marketed products of enfleurage and maceration are the well-known pomades and perfumed oils, or, of course, the floral extracts obtained therefrom by "washing" with alcohol. The method of extracting the perfume from delicate flowers by means of a non-volatile fatty solvent is of considerable importance, and is fairly ancient and of very general application in the treatment of flowers. The method in which the treatment is applied differs according to whether the odorous constituents of the flowers are capable of withstanding a more or less elevated temperature or not. And again, it differs according to whether the flower contains the whole of its potential perfume in a directly available form, so that the killing of the plant tissues by means of hot fat is a matter of indifference, or whether the perfume exists in the form of some glucosidal or similar compound, so that as fast as the fat removes the actually existing perfume material normal life processes in the flower cause the decomposition of more of the glucoside with liberation of more perfume material. In the latter case it is obvious that the flower tissues must be kept alive as long as possible, and hot fat is inadmissible. This point is exemplified in the case of *jasmin*, the perfume material of which can be extracted either by volatile solvents or by cold enfleurage. But both the yield and quality are much superior if the enfleurage process be adopted. *Nivière*, following the previous work of *Hesse*, gives the following explanation of this important difference

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(*La Parfumerie Moderne*, 1921, 225). It is quite clear that the *jasmin* flower contains one or several glucosidal bodies. He has made experiments on the effect of a preliminary hydrolysis before extraction, and in all cases obtained a higher yield when hydrolysis preceded extraction. It is customary to say that the enfleurage process yields four to five times as much as the direct extraction with a volatile solvent. But it must be remembered that, when the enfleurage pomade is washed with alcohol, a considerable amount of fatty material is dissolved, so that the true *perfume* yield by the enfleurage process is not so much higher than that by the direct extraction by petroleum ether, as is generally supposed. But it cannot be denied that the odour of the two products is very different. In the enfleurage product the presence of indol is very noticeable, and this is due to glucosidal decomposition under the influence of an enzyme.

Enfleurage and maceration processes consist in placing the flower in contact with fat (usually high-grade lard or fine beef suet) or with olive oil, and sometimes mineral oil. It is absolutely essential that the fat or oil should be of the very highest grade and as free from fatty acids as possible. The essential oil of the flower is dissolved out by the fixed oil, which eventually absorbs the whole of the perfume material from the plant. The following is, briefly, the process adopted in the maceration of flowers as detailed by Charabot ("The Present State of the Perfume Industry") :—

The fat being melted on the water bath (or the oil being heated), the flowers to be treated are added to it, and the mass is stirred to assist the extraction. The exhausted flowers are replaced by fresh ones until the fat is sufficiently charged with perfume. For that purpose a given weight of flowers is allowed for a charge of fat. The flowers, after treatment, still retain some of the perfumed fat. This is removed from them by pressing them, whilst hot, by means of presses. In this way there are obtained *pomades* when fats are employed, and *perfumed oils* when olive or mineral oils are used. The process is carried out at Grasse, principally in the case of the violet, the rose, the orange flower, and the cassie blossom.

Certain flowers, such as the *jasmin* and the *tuberose*, which contain in the free state only a portion of the odorous matters which they are capable of yielding, must, as indicated above, be treated by the process of cold enfleurage. Fat is spread on both sides of a sheet of glass surrounded by a wooden frame. On the upper surface of this apparatus, which is called a "chassis,"

the flowers are spread. Another chassis is placed on the top of the one thus charged, and so on. The flowers are thus enclosed in chambers of which the top and the bottom faces are covered with fat. The fat on the bottom surface becomes perfumed by contact and by diffusion; the odorous matters which escape are retained by the fat adhering to the upper surface.

After a certain time—the next day in the case of *jasmin*—the exhausted flowers are replaced by fresh ones, care being taken to turn the chassis over. This operation is repeated until the desired concentration is obtained. If it be required to prepare a perfumed oil instead of fat, the chassis employed differs from that described above in the fact that the sheet of glass is replaced by a metal grid which supports a thick cloth which is saturated with oil.

Whether the “maceration” process or the “enfleurage” process be employed, the odorous products are obtained in the form of pomades or perfumed oils.

The perfume is dissolved in a vehicle, fat or oil, from which it must be freed. For that purpose use is made of the property, which the odorous compounds possess, of dissolving in alcohol, which property is not possessed by the fatty matters employed. It is sufficient to beat up the pomade with alcohol for the latter to absorb the perfume without dissolving appreciable quantities of fat. Moreover, the small proportion of fat retained by the alcohol is eliminated by cooling the solution to a temperature of  $-10^{\circ}$  to  $-15^{\circ}$  C. and by subsequent filtration. The exhaustion of the fats is effected mechanically by means of *batteuses* (beating machines). Several successive washings are necessary.

These alcohol washings form the *extraits aux fleurs* or floral extracts of commerce, and the exhausted fat, from which the greater part of the perfume material has been thus extracted, is sold as *corps épuisé* for use in soap perfumery. The pomades are themselves sold under numbers, usually multiples of 12—thus, flower pomade No. 12, 24, 36, or 72; the higher the number the higher the degree of concentration claimed for the pomade. In the same way the alcoholic washings known as extracts are usually sold as triple or quadruple, and are, especially the “triple” extracts, frequently bottled off as handkerchief perfumes as they come from the manufacturer, or blended with other natural or synthetic perfumes and then marketed under fancy names.

The extraction of perfumes by means of volatile solvents is a comparatively new industry, although one which has recently made, and is still making, very rapid strides. The process was first

suggested by Robiquet in 1835, when, of course, light petroleum ether was unknown in commerce. It was not, however, turned to industrial account until successful experiments were carried out by Massignon ; but it is pre-eminently to Naudin that the process has developed into a successful industry on a large scale. To-day there are more than twenty factories in the south of France alone which carry on the extraction of flower perfumes by this method. In 1879 Naudin took out his master patent (No. 130137, French Patent) on a " New Commercial Method of extracting Perfumes *in vacuo* and in the Cold." The apparatus therein described consisted essentially of an extractor formed of a closed receptacle with a pannier for holding the flowers, with a decanter and an evaporator. The extract was charged with the flowers and solvent, and the cover replaced and sealed. After contact with the flowers for about a quarter of an hour, that part now charged with perfume was directed by means of diminished pressure into the decanter, where the water from the flowers separates. The solvent eventually found its way into the evaporator by gravity. The solvent was then evaporated at the ordinary temperature *in vacuo*, so as to avoid all heating effects. The condenser was kept at a very low temperature by artificial means. As regards solvents, Naudin suggested ethyl chloride and the lighter fractions of American petroleum. (Interesting accounts of Naudin's work will be found in the *Bull. Soc. Chim.*, 1882, 38, 586, and in the *Moniteur Scientifique*, February, 1883, 174.) Naudin established the validity of his patent in the French Court of Appeal, but the expenses of the litigation nearly ruined him, and he abandoned the patent in disgust, and it may be regarded as the substantial basis of all methods in use to-day in France. The essential oil and resins of the plant are the only perfume bearers, and in choosing a solvent for extraction purposes the following points have to be carefully borne in mind :—

(1) It must dissolve out the whole of the odour-bearing substances present in the plant.

(2) It must be perfectly neutral and inert and have no chemical action whatsoever on the odorous substances.

(3) It should dissolve as little else as possible from the plant tissues.

(4) It must distil steadily within such limits of temperature that the perfume material is not damaged by the heat necessary for distillation, and so that the perfume material should not itself volatilise with the solvent and so cause considerable loss.

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(5) It must leave no residue and no odour behind on evaporation.

The principle of extraction is more or less that of a Soxhlet extractor, so that the process is continuous. When the whole of the perfume is extracted by the solvent—very low boiling petroleum ether being the most suitable for nearly all purposes—the solvent is recovered, and the residue consists of the essential oil, resinous matter, fat, wax and colouring matter. This raw material is usually solid or semi-solid on account of the wax and fat present; hence the name “concretes.” But as the wax and fat are insoluble in alcohol, it is obvious that the employment of these concretes gives rise to considerable inconvenience, usually accompanied by a loss of alcohol, as perfect filtration is necessary to separate the insoluble waxy matters. Charabot has worked very successfully in the direction of removing this inconvenience. He gives the following brief summary of the outlines of improvements which lead one from the concretes to the so-called “absolutes” or “liquid flower oils,” as they are sometimes called (“The Present State of the Perfume Industry,” Paris, 1909, p. 8):—

“The period at which the process of extraction of perfumes by volatile solvents entered into the region of industrial realities, some fifteen years ago, coincided exactly with the time of my first researches at the Sorbonne, in the laboratory of Charles Friedel, in the same laboratory where, first under the direction of Wurtz and subsequently under that of my illustrious and lamented master, such a strenuous and glorious struggle had been maintained for the definite triumph of the splendid atomic theory, thanks to which organic chemistry has produced the marvellous results which are so evident to all. The industry of the artificial perfumes, on the morrow of the discovery of ionone, had just taken a new step in advance, and the synthetic products were beginning to claim their place in compositions of the finest quality. Perfumery then had need of natural raw materials sufficiently powerful, and consequently sufficiently concentrated, not to be dominated, crushed out of existence by the chemical perfumes. These latter were capable of imparting, even to the most delicate compositions, valuable characters of originality and fixity, but only on the express condition that they can be sufficiently dominated by products derived from flowers, which are the only ones which can impart delicacy and sweetness. It was this necessity, accentuated still more by the tendency of fashion towards powerful and tenacious perfumes, which struck me,

together with the inconveniences involved by the first products obtained by means of volatile solvents. And thus my researches were directed towards the obtaining of the perfumes of flowers in the form of products both powerful and soluble in alcohol. They soon led to a satisfactory solution and the preparation of products conforming with the desiderata mentioned above. Since then we have been able to substitute for the first processes which I invented methods which are more perfect because they have been deduced from the accumulation of acquired knowledge both on the composition of the odorous matters and on their successive states in the plant. And these methods, made appropriate to the treatment of each flower, have enabled us, by employing the solvents in a suitable manner, to leave the vegetable wax, the inodorous substance which is insoluble in alcohol, behind, and to extract solely and completely the odorous principles in the form of products entirely soluble in alcohol. These products, the *absolute flower oils*, are consequently extremely convenient to use, since it is only necessary to pour them into alcohol to obtain a clear solution of any concentration that may be desired.

“But, being extremely powerful products, they have a somewhat high value, and their prices differ from one flower to another. In order to have for each flower products which are comparable among themselves, and which can be sold at a price which makes them more convenient to handle, it was most desirable that these products should be *standardised in strength and of uniformly excellent quality*.

“The form of *liquid flower oils* is the most advantageous from all points of view for the utilisation of the odorous products extracted from plants. In addition to all the qualities enumerated above, the liquid flower oils possess the very important advantage of presenting no variation from one crop to another, since they do not contain, like the solid flower oils, the odourless wax, the proportion of which is essentially variable according to the season.”

Amongst the flowers which are regularly treated in this manner may be mentioned rose, orange, jasmin, tuberose, cassie, jonquil, narcissus, carnation, mignonette, broom, mimosa, and violet.

The exact method by which the insoluble wax is removed from the concretes differs according to the manufacturer, but in general it consists of agitating the concrete with alcohol in suitable machines (*batteuses*) and removing the insoluble matter by filtration, and then cooling the filtrate to 20° below zero in order

to cause the last traces of dissolved wax to separate. The "absolute" oil is separated either by removing the alcohol *in vacuo* or by salting out and separating. Attempts, partially successful, to remove all colour from these absolutes have been made by distilling the oil from the absolute. Owing to the intense strength of these oils, they are frequently standardised with a neutral body so that they are perfectly soluble in alcohol, and a whole series of absolutes by one maker may have identical strengths in relation to the finished product in which it is to be used.

**FACE POWDERS.**—Toilet powders are merely mixtures of certain white powders, tinted or untinted as desired, and perfumed to taste. The absolute essentials of a satisfactory face powder are (1) freedom from grittiness, (2) the desired amount of adherence to the skin, (3) satisfactory colour and perfume. For the first, the most perfect grinding (where grinding is necessary) and sifting must be employed, so that the resulting powder be absolutely impalpable. In order to cause the powder to adhere to the skin, a careful choice of the main ingredient is necessary, as well as the discreet employment of small quantities of a subsidiary substance. For example, wheat starch does not adhere to the skin nearly so well as does maize starch. The questions of colour and perfume are, of course, matters of taste which do not require discussion here.

The principal constituent of the older-fashioned, and still highly esteemed, face powders is starch powder, the most usually employed varieties being maize and rice starch. The old-fashioned violet powder was essentially a mixture of starch and powdered orris root with a trace of perfume.

These old-fashioned powders have been to a certain extent replaced by the more modern "talc" or "talcum" powders, which are based on finely powdered talc (*q.v.*).

To these powders a small quantity of particularly adherent substances is commonly added, amongst which are zinc oxide, bismuth carbonate, subnitrate and oxychloride, zinc or magnesium stearates, kaolin, and kieselguhr.

The mineral substances usually incorporated in these powders, apart from those above mentioned, are precipitated chalk, light magnesium carbonate, but scarcely barium sulphate, as is often stated, except occasionally in very small quantities, as it is so extremely dense.

Formulae by the hundred for these preparations are to be found in all the text-books on practical perfumery. (See also *P. & E. O. R.*, 1923, 442.)

**FAGARA XANTHOXYLOIDES.**—See “Xanthoxylum Oils.”

**FARNESAL.**—See “Farnesol.”

**FARNESOL.**—This body is an aliphatic sesquiterpene alcohol, of the formula  $C_{15}H_{26}O$ . It occurs in the essential oils of ambrette seed, acacia (cassie), lime flowers, mignonette, and lilac flowers. In ambrette seed oil it is present to some extent as the ester of palmitic and other acids. In order to prepare it from this oil, the oil should first be saponified, after dilution with alcohol, by heating it with alcoholic potash under a reflux condenser for eight to ten hours. The alcohol is removed by distillation, and the residue washed with water. The crude farnesol is distilled in a current of steam, and purified by conversion into its phthalic acid ester. It is present in ambrette seeds to the extent of about 0.1 per cent., associated with a little decylic alcohol. It is a fragrant oil of apparently very little odour, but in dilute alcoholic solution it has a sweet odour recalling that of a mixture of lily of the valley and cedarwood oil. It has the following characters:—

Boiling point at 10 mm.	160°
Specific gravity	0.887
Optical rotation	0°
Refractive index	1.4881

The constitution of farnesol has been established by Kirschbaum (*Berichte*, 1913, 46, 1732), who has also prepared it synthetically by acting upon dihydropseudoionone with magnesium bromoacetic ester. The resulting hydroxydihydrofarnesic ester is heated with acetic anhydride and sodium acetate, when farnesic methyl ether results, from which farnesol is set free. (See also Ruzicka, *Helv. Chim. Act.*, 1923, 6, 492, for the complete synthesis of farnesol.)

If farnesol be oxidised by chromic acid mixture, the corresponding aldehyde, farnesal  $C_{15}H_{24}O$ , results. This is an odorous body having a specific gravity 0.895, refractive index 1.4995, and boiling at 174° at 14 mm. It forms a crystalline semicarbazone melting at 133° to 135°. Farnesol forms an acetic ester, farnesyl acetate, boiling at 170° at 10 mm. pressure.

Farnesol is of considerable value in perfumery if used with discretion.



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Ruzicka (*loc. cit.*) gives the following as the characters of the specimens of farnesol prepared from the sources quoted :—

Source of farnesol.	Specific gravity.	Refractive index.
Ambrette seed oil .	0.885 at 18° ..	1.4881
Neroli oil . . .	0.893 at 15° ..	1.4899
Citronella oil . .	0.895 „ ..	—
Java cananga oil .	0.895 „ ..	—
Synthetic . . .	0.891 at 20° ..	1.4890
<i>d</i> -Nerolidol . . .	0.895 at 18° ..	1.4924 at 18°

It is probable that some of these specimens represent geometrical isomerides.

Naef & Co. have patented the preparation of farnesol by the action of acetic acid upon nerolidol, or by the oxidation of nerolidol to farnesal by means of chromium trioxide and reduction of the farnesal (International Convention date, March 22nd, 1923). (See “Nerolidol.”)

**FENCHONE.**—This ketonic compound, of the formula  $C_{10}H_{16}O$ , is found in bitter fennel oil, and also to a small extent in the oil of *Lavandula Stoechas*. In both these oils it exists as *dextro*-fenchone, but is also found as *laevo*-fenchone in thuja leaf oil. It is an oil of characteristic sharp odour, having the following characters :—

Boiling point . . . .	192°–193°
Melting point . . . .	+ 5° to + 6°
Specific gravity . . . .	0.950
Refractive index . . . .	1.4630
Specific rotation . . . .	about $\pm 70^\circ$

By reduction fenchone is converted into fenchyl alcohol, melting at 45°. Fenchyl alcohol always has an optical rotation opposite to that of the fenchone from which it is prepared.

**FENCHYL ALCOHOL.**—The chemistry of fenchyl alcohol is still in a very unsettled condition, on account of the very similar characters possessed by bodies which are probably isomeric and difficult to separate in a state of purity. The naturally occurring body known as fenchyl alcohol has only been found in the essential oil from the root wood of *Pinus palustris*. Two artificial fenchyl alcohols have been prepared by Schimmel & Co. (*Report*, October, 1898, 49; April, 1900, 55, 60) which are described as fenchyl alcohol and isofenchyl alcohol. They have the following characters :—

	Fenchyl alcohol.	Isofenchyl alcohol.
Melting point . . . .	45° ..	61° to 62°
Boiling point . . . .	92° at 11 mm. ..	98° at 13 mm.
Boiling point of acetic ester .	88° at 10 mm. ..	99° at 14 mm.

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**FENNEL OIL.**—This oil is the product of the distillation of the fruit of *Fœniculum vulgare*, an umbelliferous plant grown in various parts of Europe, not only for its fruits, but also for its edible root. It is found in most parts of Europe, being especially common on the Mediterranean littoral, in Germany, Moravia, Galicia, Bukovina, Moldavia, Roumania, France, Italy, and Macedonia. It is also found freely in Persia, India, and Japan. Two special types of oils are recognised in commerce, known as "sweet" and "bitter" fennel. The sweet fennel oil is the product of the plant frequently known as *Fœniculum dulce*, which is, in all probability, only a variety of the ordinary wild plant. It is also known as Roman fennel. The ordinary wild bitter fennel, growing chiefly in France, Spain, Algeria, and Japan, yields the so-called bitter fennel oil.

The yield of ordinary or cultivated bitter fennel oil depends on the district from which the fruits are collected, varying from 3 to 5·5 per cent. According to Schimmel & Co., the principal commercial varieties yield the following amounts of essential oil :—

	Per cent.
Saxon fennel (Lützen) . . . . .	4·4–5·5
Galician . . . . .	4–6
Moravian . . . . .	3
Roumanian . . . . .	4·6

The distillation residues are of great value as fodder for cattle. When dried, they contain from 14 to 22 per cent. of proteids, and 12 to 18·5 per cent. of fat. Normal bitter fennel oil has the following characters :—

Specific gravity . . . . .	0·965–0·977
Optical rotation . . . . .	+ 11° to + 24°
Refractive index . . . . .	1·5280–1·5380

A good quality oil congeals within the limits + 5° to + 10°. The oil is soluble in its own volume of 90 per cent. alcohol.

The principal constituent of the oil is anethol, which accounts for its odour resembling aniseed oil. It is present to the extent of 50 to 60 per cent. in high grade oils. It also contains fenchone (*q.v.*), which is absent from the so-called sweet fennel oil. The terpenes pinene, camphene, phellandrene and dipentene are also present, as well as small quantities of methyl-chavicol, anisic aldehyde, and anisic acid.

The oil obtained from the sweet or Roman fennel, which is obtained to the extent of from 2 to 3 per cent. from the seed

grown in Southern France, has a high anethol content, and is free from fenchone. It has a specific gravity 0.976 to 0.980; optical rotation  $+5^{\circ}$  to  $+16^{\circ} 30'$ ; and congealing point  $+10^{\circ}$  to  $+14.5^{\circ}$ .

Macedonian fennel oil resembles the French sweet fennel oil. It has a sweetish taste, due to its high anethol content and its freedom from fenchone. The yield is from 1.7 to 2.8 per cent. The oil has a specific gravity 0.970 to 0.980; optical rotation  $+5^{\circ}$  to  $+12^{\circ}$ ; and congealing point  $+7^{\circ}$  to  $+12^{\circ}$ . Sicilian fennel oil is distilled from *Foeniculum piperitum*, known in Sicily as ass's fennel (*Finocchio d' asino*). The fruits are used as a spice in southern Italy. They yield about 3 per cent. of essential oil, of specific gravity about 0.950, containing little or no anethol, as it does not congeal even at  $-5^{\circ}$ .

The wild growing plants of the bitter fennel, found in France, Spain and Algiers, yield about 4 per cent. of essential oil of specific gravity 0.905 to 0.925, and optical rotation  $+40^{\circ}$  to  $+68^{\circ}$ . The principal constituent of this wild oil is the terpene *dextro-a*-phellandrene. It also probably contains the compound *di-para*-methoxy-stilbene, melting at  $214^{\circ}$  to  $215^{\circ}$ .

The Japanese oil is distilled from very small fruits, which are known as Japanese aniseed. The oil very closely resembles the ordinary German oil.

Tardy ("Étude analytique sur quelques essences du genre anisique," Thèse, Paris, 1902, p. 23) has examined the oil from Algerian bitter fennel. It had a specific gravity 0.991; and optical rotation,  $+62^{\circ}$ . In it were identified pinene, phellandrene, fenchone, methyl-chavicol, anethol, a sesquiterpene, and, probably, thymohydroquinone.

The herb yields an oil which differs from that of the fruits, but this oil has not been fully examined. The oil distilled, however, from the herb *Foeniculum capillaceum* in Java (from the leaves and stems) was found (*Jaarb. dep. Land. Ned. Ind. Batavia*, 1907, 45) to have a specific gravity 0.970; optical rotation,  $+40^{\circ} 50'$ ; and congealing point,  $12.8^{\circ}$ . Anethol and methyl-chavicol are present in the oil.

The fruits of the water fennel *Oenanthe Phellandrium* yield from 1 to 2.5 per cent. of essential oil. This has a powerful and penetrating odour, and has the following characteristics: specific gravity, 0.850 to 0.890; optical rotation,  $+12^{\circ}$  to  $+19^{\circ}$ ; refractive index, 1.4840 to 1.4950. It consists very largely of the terpene phellandrene. It also contains an aldehyde  $C_{10}H_{16}O$

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which has been named phellandral ; an alcohol  $C_{10}H_{20}O$ , termed androl, and an alcohol of unknown constitution.

Sage and Goodale (*P. & E. O. R.*, 1922, 18) have examined a Spanish fennel oil, the yield being 3.75 per cent.

The oil has a sweet taste and good flavour, and possesses the following characters :—

• Specific gravity at 15.5° . . . . .	0.9638
Specific gravity at 25.0° . . . . .	0.9571
Refractive index at 25.0° . . . . .	1.5243
Optical rotation at 20.0° . . . . .	+ 17.8°
Solubility in 80 per cent. alcohol . . . . .	1 in 5
Congeaing point . . . . .	— 3.5°

By fractionally distilling the oil, under ordinary atmospheric pressure, they obtained the following yields :—

	Per cent.
Distilling between 180° and 200° . . . . .	7
"      "      202°      "      210° . . . . .	18
"      "      210°      "      225° . . . . .	57
"      "      225°      "      235° . . . . .	15
"      above 235° . . . . .	3

The low congealing point of the entire oil shows that it contains a low proportion of anethol, but the fraction distilling between 225° and 235° was found to have a congealing point of 13.3°, and the separated solid was undoubtedly anethol.

They attempted the oximation of the oil and of the lower boiling fractions, but found practically no ketone present, and the yields being under 2 per cent. indicate the absence of notable proportions of fenchone. The oil yielded reactions indicating the presence of some phellandrene, but the proportion must have been quite low.

It is apparent from these experiments that these fruits, as grown in Spain, do not yield an oil containing any notable proportion of fenchone, and that the amount of anethol cannot be considered sufficiently high to make the oil as good for medicinal purposes as oil from Saxon or Galician fennel.

**FERULA SUMBUL, OIL OF.**—See "Sumbul Oil."

**FEVERFEW OIL.**—The oil of *Pyrethrum parthenium* is distilled on a small scale. It contains a terpene, borneol, and bornyl esters. Its specific gravity is from 0.900 to 0.960.

**FIXATIVES.**—The question of the lasting power of perfumes is one which is of the highest importance to the perfumer to-day, as the general tendency has grown to requiring perfumes which

shall be lasting and tenacious, as differentiated from those which, however sweet, volatilise very rapidly. To-day it is necessary to recognise that there are two very sharply differentiated classes of fixatives. There are, in the first place, those which are so nearly odourless, either *per se* or on account of the minute quantities necessary in practice, and so act almost entirely as pure fixatives only; and, in the second place, there are those powerful fixatives which are also highly odorous themselves, so that they modify the odour of the other constituents of the perfume to a more or less noticeable extent, and to that extent become active odour bearers in the perfume itself, as well as mere fixatives. At one end of this series there are, of course, those whose contribution to the odour is but slight, and again, at the other end of the series, those that definitely contribute to the odour in such a way that, as the more volatile constituents evaporate, the odour of the "fixative" becomes more pronounced.

It has been said that the ideal fixative is one which will equalise the differing rates of evaporation of the various odorous constituents of the perfume. This, however, is scientifically quite inaccurate, as the alteration in the vapour tension of one liquid, when mixed with another liquid of different vapour tension, is a mathematical matter depending on the individual liquids themselves. For example, if bergamot oil, neroli oil, and lavender oil in an eau de Cologne would (to put it in popular form) evaporate in A, B and C hours respectively, the addition of a given fixative will cause the evaporation periods to become  $A + X$ ,  $B + X^1$ , and  $C + X^2$  respectively, where X,  $X^1$  and  $X^2$  may be different, and in general  $A + X$ ,  $B + X^1$ , and  $C + X^2$  will almost certainly be different. The *real* effect will have been a general prolongation of the whole of the perfume, which will, during the evaporation period, gradually change in nature according to the loss of any given constituent. The gradual development of the public taste in favour of tenacious perfumes has led to the manufacture of numerous artificial fixatives, and to-day it is correct to say that hardly any perfume formula can be considered complete without its including a recognised fixative. Fixatives may broadly be classified as follows:—

- (1) Pure fixatives, which do little else than render the perfume less fugitive.
- (2) Fixatives having a pleasant odour, which modify the perfume itself in a noticeable (more or less) degree.
- (3) Fixatives having a disagreeable odour, which are used in

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minute quantity and which, in the very dilute solution in which they are used, become insensibly agreeable, like "garlic smeared round the salad bowl."

Deodorisation of alcohol is, of course, a misnomer in regard to fixation. The use of any ordinary fixative on an alcohol which has an undesirable odour merely acts as a cover, and does not in any way destroy the bad odour. In fact, it is no exaggeration to say that more rubbish has been written in regard to the question of fixatives than in most branches of practical perfumery. No fixative will "overcome" the effects of synthetics. The truth is that these "effects" do not require overcoming. If the perfumer wants a perfume of overpowering strength, as certain classes demand, he will use an excess of synthetics and get his powerful odour. If he does not want this, he will use minute quantities of synthetics which do not, when properly used, produce any result which requires the words "harsh" or "chemical" to describe it. Fixatives do not enter into this question at all.

The classes of fixatives given above are recruited from three main sources: (1) animal substances; (2) vegetable oils, resins and balsams; (3) artificial or synthetic compounds.

Fixatives derived from animal sources have long been held in high esteem by perfumers. The bodies employed for this purpose are musk, ambergris, civet, and castor. It has been seriously suggested that the popular use of these animal perfumes was initially due to what the French have named '*l'odeur de chair*,' and that the animal perfume had a sex attraction. This suggestion will hardly bear examination. There is no doubt that the four main animal fixatives do *fix* the perfume exceedingly well and, when used with discretion, do not interfere with the main floral odour when such is being used. For example, the highly disagreeable civet, which in the natural state has a foul faecal odour, is used in the finest white rose perfumes manufactured, and at no stage of the evaporation of the perfume does any disagreeable civet odour become apparent.

The principal natural vegetable fixatives are the balsams, gum-resins, and very high-boiling essential oils whose constituents are, very frequently, sesquiterpenes and sesquiterpene alcohols. Amongst artificial substances used as fixatives there are a number which are practically *only* fixatives, although they may be used as solvents as well, for example, benzyl benzoate, with its high boiling point and its useful solvent action on artificial musk; and there are a number which have very marked odours as well

as fixative properties. For example, diphenyl oxide is sometimes referred to as a fixative. In fact, it is a high-boiling substance with a powerful geranium odour, and is more correctly described as an artificial geranium perfume of great lasting power. For an exhaustive list of substances classed as fixatives, but which should be examined carefully in regard to the real proportion between odour value, reference may be made to the following works: Durvelle, "The Preparation of Perfumes and Cosmetics" (London: Scott, Greenwood & Co.), 1923, pp. 124-126; and Poucher, "Perfumes and Cosmetics" (London: Chapman and Hall), 1923, pp. 201-203.

**FLEABANE OIL.**—The fresh flowering herb *Erigeron canadensis* yields about 0.5 per cent. of an aromatic essential oil known as fleabane oil. It contains limonene, terpineol, and traces of citronellal, and has a specific gravity 0.855 to 0.870; optical rotation, + 52° to + 81°; acid value, 0.15; and ester value, 34 to 109.

**FLORIDA WATER.**—This perfume, which, of course, is not protected with a proprietary name, is one of exceedingly popular character in America, and, to a smaller extent, in far Eastern countries that import it. It is, in the United States, largely what lavender water is in England. It is a toilet perfume somewhat resembling a mixture of lavender water and eau de Cologne, rounded off with one or more of the following bodies; cassia oil (or cinnamon oil, or cinnamic aldehyde); clove oil (or pimento oil, bay oil, or eugenol); and lemongrass oil.

**FOIN-COUPÉ.**—This popular type of perfume is supposed to reproduce the odour of new-mown hay. It is invariably based on coumarin, modified by lavender, bergamot, and other perfumes, according to the exact note the perfumer wishes to give to his product. The odour of true new-mown hay is due more to the sweet-scented grass known as *Anthoxanthum odoratum* than to any other grass, although many others contribute to it. Several different types of clover, of course, also add to the fragrance of the hayfield odour. This odour is probably the result of glucosidal decomposition of constituents present in the plants, resulting in the formation of a little coumarin. (See *American Perfumer*, 1922, 57.)

**FORMYLATION.**—See "Alcohols, Determination of."

**FRACTIONAL SAPONIFICATION.**—See "Esters, Artificial."

FRAGAROL.—See “ $\beta$ -Naphthol-butyl Ether.”

FRANGIPANI.—(See also “Plumiera.”)—This name is applied to a particular type of fancy perfume which, at one time, achieved great popularity in this country. The name is said to have been derived from the office held by an old Roman family, namely, of breaking the bread (the meaning of the word) in the celebration of holy communion. A descendant of this family, which appears to have adopted the official title into its name, is said to have introduced a special perfume for gloves which is, at least by legend, the lineal ancestor of the modern “Frangipani” (see below). The name was, at all events, given by French colonists in the West Indies to the odorous plants *Plumiera rubra* and *Plumiera alba*. These trees belong to the natural order *Apocynaceæ*. They are natives of Peru and other parts of South America, and are found in several of the West Indian islands. The genus was named by Tournefort in honour of Charles Plumier, a Franciscan traveller in South America and author of several works on botany. *Plumiera rubra* is called by the French in the West Indies *Frangipanie rouge*, and also “red jasmin.” It is a tree from 12 to 20 feet in height, yielding highly odorous flowers, which are used by the native women to perfume their linen as we use lavender flowers. Several other varieties are cultivated, and are highly odorous. Amongst them is *Plumiera acutifolia*, a plant which is cultivated in cemeteries in the Philippine Islands. The flowers have a marked “frangipani” odour, but no essential oil has been obtained from them. Bacon (*Philip. Jour. Science*, 1909, 4, A, 131) showed that if the flowers be heated to 40° the odour was destroyed. An extract was obtained by means of petroleum ether with the typical odour of frangipani, although no essential oil could be obtained.

But the flowers of *Plumiera acutifolia* exhale a very pleasant and highly esteemed perfume. Descourtilz, in his “Flora of the Antilles,” praises with voluble enthusiasm this “sweet odour,” comparable, he says, with that of the tuberose or gardenia, and “much in demand by the young girls on fête-days.” The creoles place the freshly gathered flowers of the frangipani in their linen and in their rooms, and the planters, to honour their guests, often strew the beds with these blossoms. This very penetrating perfume still persists for a fairly long time after the flower has been separated from the tree on which it grew. It was doubtless in imitation of this that boquets *à la frangipane* were formerly compounded.



This species is cultivated in India, but its origin is Central America, probably somewhere about Mexico. It is not indigenous in tropical Asia, as A. de Candolle believed. In India the flowers are laid in the temples and on the graves, as offerings. In the Philippines, the *Plumiera* is frequently used as a "cemetery tree"; they plant slips which take root easily and grow rapidly.

The following interesting account of this perfume is due to Daniel Hanbury and was written in 1859, and is abstracted in the *Perfumery and Essential Oil Record* (1915, 238) as follows:—

Frangipani is the name of a very ancient, aristocratic Roman family dating from the eleventh century, a member of which, Cencio Frangipani, became a leader of the Ghibeline faction against the Guelphs during the century following, and many times since then has the family figured in the romantic history of Italy. On board the *Santa Maria* with Columbus was one Mercurio Frangipani, and in the Papal army assisting the French King Charles IX. against the Huguenots was a Mutio Frangipani. The grandson of the latter was the Marquis Frangipani, Maréchal des Armées of Louis XIII., and he it was who turned his ingenuity to a very unmilitary invention, a method of perfuming gloves, which when so scented were known as "Frangipani gloves." The authority is Ménage, in his "*Origini della Lingua Italiana*," published at Geneva in 1685; he says "Da uno di que Signori Frangipani (l'abbiam veduto qui in Parigi) furono chiamati certi guanti profumati, *Guanti di Frangipani*" [from one of which Frangipani (I saw him here in Paris) were named certain perfumed gloves, "Frangipani gloves"]. From another old record, Le Laboureur's "*Mémoires de Castelnau*," we learn that a brother of the Marquis was also associated with the invention: "Ce dernier Marquis Frangipani, et son frère mort auparavant luy, inventerent la composition du parfum et des odeurs qui retiennent encore le nom de Frangipane."

In an extraordinary work entitled "Frangipani's Ring: an Event in the Life of Henry Thode," translated from the German and published in London by John Macqueen in 1904, reference is made to a work entitled "Chronicle of the Island of Veglia and of the Frangipani Family upon this Island," by Antonio Vinciguerra, Secretary of the Senate and the Republic of Venice, a work mentioned in the Catalogue of Manuscripts in St. Mark's Library in Venice. Thode, attempting to trace the origin of the family, writes of it as follows:—

"A stalwart race, inhabiting strong castles in Croatia, with its

ancestral seat in Modrusa and Segna (Zengg), which was given it in fief by Bela III. in 1260. Driven about by their passions through the following centuries to ambitious scheming, wild undertakings, and outrageously violent deeds; forced by their terrifying superstitions to take refuge in fantastic religious devotions; heroic and faithless, unruly and calculating in capricious change, they wasted their turbulent lives in warring with their neighbours and with themselves.

"Whence the race originally came cannot now, with any certainty, be stated. One authority contends that its home from the first was in Croatia, and that the name, literally 'Frankopan,' means 'Francis the Lord'; others assert that it was a severed branch of the Roman family of the Frangipani, whose annals are stained with the dastardly betrayal of the last Konradin of Hohenstaufen by the Lord of Asturia, John Frangipani, and with the treacherous assassination of Duke Frederick the Warrior. Contrary to this, the authors of the Venetian genealogies, and among them the earliest, so far as I know, Francesco Venier and Zancarola, relate in their chronicle (now in St. Mark's Library) that in former times a family of the Frangipani came from Ravenna to Venice, where they became members of the Great Council, and that, with the death of Giovanni, who held a position in the Mint, this line became extinct in 1347; they also hold that from these Ravenese-Venetian Frangipanis the Croatian branch originally sprang."

It will be noted that the Italian writers mention only perfumed gloves, whereas La Laboureur speaks of "*la composition du parfum et des odeurs*," which would appear to include some essence, powder or pomade. This much is certain, however, that certain compositions as *pomade*, *essence* and *powder*, styled *Frangipani* or *Frangipane*, were sold by perfumers down to a century ago, when they appear to have fallen into disuse. A revival of certain perfumes bearing the name occurred in the 'fifties, and formulæ appeared in Piesse's "*Art of Perfumery*," London, 1856, and Celnart's "*Nouveau Manuel Complet du Parfumeur*," Paris, 1854. The various formulæ to be found vary so much among themselves that, obviously, they cannot all represent the original. "*Pharmaceutical Formulas*" (MacEwan, 1914) gives three such recipes from which to choose, and judging from their constituents one might describe them as dainty, rich, and heavy respectively, according to the predominance of floral extracts, otto of rose, sandalwood, civet, ambergris, and musk.

It may be taken for granted that the basic odour of "frangipani" perfumes to-day is that of jasmin, modified with substances having "heavy odours."

**FRANKINCENSE.**—See "Boswellia Resin."

**FUMIGATING PASTILLES.**—Fumigating pastilles are usually moulded into the shape of cones, and are prepared from pastes from which the water is driven off after the pastilles have been cut into shape by appropriate moulds. These pastes are made up from selected varieties of charcoal, with potassium nitrate to ensure even and continuous burning, and mixed aromatic gums and balsams, with other aromatic volatile substances to give a highly aromatic odour on burning. They are, in fact, little else than "moulded incense." Frequently a little powdered cascarilla bark or other substance burning with an aromatic odour, is added. Benzoin and storax are the usual balsamic substances employed, and powdered cascarilla, cinnamon, cloves, cedar wood and vetiver root are the usual vegetable powders used. Vanillin, heliotropin, and the oils of cedarwood and sandalwood are the usual perfume additives. Charcoal is usually present to the extent of 25 to 50 per cent., and potassium nitrate from .5 to 7.5 per cent. Occasionally the charcoal is replaced by red sandalwood, the pastilles being red instead of black in colour; or by fine white pine sawdust, when the pastilles are nearly white. The exact formulæ for the finest odours are, of course, trade secrets.

**FUSANUS SPICATUS, OIL OF.**—The so-called Western Australian sandalwood oil is the distillate of the wood of *Fusanus spicatus*, a tree originally known as *Santalum cygnorum*. The oil resembles true sandalwood oil in odour, and contains similar, but not identical, constituents. It is of very great value to the perfumer, and is largely employed for perfuming soap. The natural oil has the following characters:—

Specific gravity	. . . . .	0.957 to 0.972
Optical rotation	. . . . .	+ 1° to - 8°
Refractive index	. . . . .	1.5015 to 1.5100
Total alcohols (as $C_{15}H_{24}O$ )	. . . . .	65 to 78 per cent.

The oil is, however, fractionated so as to contain up to 95 per cent. of alcohols, and is obtainable in this condition on the market.

It has recently been fully investigated by Sanjiva Rao and Sudborough (*Journal of the Indian Institute of Science*, vol. v., xii.,

1923, 163). These authorities give the following account of the tree, its wood, and the essential oil :—

The sandalwood, although only a tree or shrub, is an important factor in the timber industry of Western Australia. The species is somewhat peculiar in its appearance, and certainly has more of the character of a large bush than of a tree proper. It has a low, depressed habit, and is consequently decidedly branchy and heavily topped. It is seldom more than 8 inches in diameter and 12 to 18 feet high, with stems 8 to 10 feet long.

The value of the wood exported from Australia is given as £96,050 in 1882, when the price was £10 per ton, and £117,072 in 1918–19, when the price of wood was £13 per ton. Most of the wood finds its way to China and, to a small extent, to other Eastern countries. Within recent years increasing quantities of wood have been imported into India as shown by the following figures :—

Year.	1914–15	1916–17	1917–18	1918–19	1920–21 10 months
Value of imported wood	£8,372	£11,080	£16,080	£29,860	£30,370

The yield of oil from the wood is 2 to 3 per cent. as compared with a yield of 5 to 6 per cent. for the genuine East Indian sandalwood (*Santalum album*). The oil was first distilled in 1875 by Messrs. Schimmel & Co., of Leipzig, and subsequently the distillation was undertaken in Fremantle. [And also near Albany, where a distillery existed in 1900. (E. J. P.).] In 1918–19 3,720 lb. of oil were distilled in Australia, and found a market in Australia and Java as a substitute for East Indian sandalwood oil in both perfumery and medicine.

The following are the values obtained on the analysis of four samples of the natural oil :—

	A	B	C	D
Specific gravity at 15/15° .	0.957	0.970	0.958	0.972
Refractive index at 25° .	1.5019	1.5040	1.5030	1.510
Optical rotation at 25° .	— 7.7°	— 0.7°	— 0.25°	— 0.87°
Solubility in six parts of 70 per cent. (by volume) alcohol at 20° .	Insoluble	Insoluble	Insoluble	Insoluble
Total alcohols calculated as santalol, C <sub>15</sub> H <sub>24</sub> O .	80.0	69.3	76.3	78.5
Esters calculated as santalyl acetate . . . . .	2.4	6.5	2.3	3.8
Acid value . . . . .	—	5.0	2.9	4.2

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A sample of oil B was distilled under atmospheric pressure, and three fractions collected and examined ; the following values were obtained :—

No. of fraction.	Boiling point.	Weight in grams.	Percentage weight.	$n_D^{25}$	Optical rotation at 25°.
1	258–280°	3.2	21.3	1.4994	— 2.0
2	280–285°	3.1	20.0	1.5014	— 1.1
3	285–309°	7.0	46.6	1.5079	+ 1.2

During the distillation, fumes and an empyreumatic odour were observed, indicating partial decomposition.

Two hundred grams of the original oil were saponified with alcoholic potash, washed, dried with anhydrous potassium carbonate, and subjected to fractional distillation under a pressure of 9 to 10 mm., using a pear-shaped fractionating column with five pears.

From 180 grams of saponified oil, seventeen fractions and a residue were obtained, and the analytical data for these fractions were as follows :—

No. of fraction.	Pressure in mm.	Temp. in degrees C.	Weight in grams.	Optical rotation at 25°.	Refractive index at 25°.	Soluble in 6 vols. of 70 per cent. alcohol.	Alcohol $C_{15}H_{24}O$ per cent.
1	13	135–150	6.4	— 4.8	1.4942	Insoluble	—
2	13	150–153	9.4	— 4.6	1.4963	"	—
3	13	153–158	10.5	— 4.2	1.5001	"	—
4	13	153–158	8.6	— 3.6	1.5000	"	—
5	13	158–160	6.5	— 3.5	1.5006	"	—
6	13	160–164	5.1	— 2.6	1.5004	"	—
7	13	160–164	12.1	— 1.6	1.5022	Clear at 60°	—
8	9–10	164–166	8.9	— 1.3	1.5034	" 45°	73.3
9	9–10	164–166	6.4	— 1.1	1.5041	" 35°	—
10	9–10	164–166	10.3	— 1.0	1.5048	" 26°	—
11	9–10	166–168	8.4	— 0.9	1.5059	" 20°	—
12	9–10	166–168	7.1	— 0.6	1.5065	" 14°	—
13	9–10	166–168	8.2	— 0.3	1.5067	" 13°	87.9
14	9–10	166–168	6.5	+ 0.3	1.5092	" 6°	—
15	9–10	168–172	6.6	+ 1.5	1.5101	" 2°	95.1
16	9–10	168–172	7.0	+ 1.6	1.5103	" 3°	—
17	9–10	168–172	22.2	+ 1.4	1.5096	" 28°	87.9
Residue	—	—	25.2	—	—	—	—

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It was found that the oil contained two isomeric sesquiterpene alcohols, to which the name fusanol has been applied. The characters of these alcohols are here compared with those of the isomeric santalols from true sandalwood oil :—

	$\alpha$ -Fusanol.	$\beta$ -Fusanol.	$\alpha$ -Santalol.	$\beta$ -Santalol.
Boiling point at 5 mm. . .	146-148°	153-155°	148°	158°
$d_{15}^{15}$ . .	0.9775	0.9753	0.979	0.973
$n_D^{25}$ . .	1.5060	1.5100	1.4968	1.5067
$\alpha_D^{25}$ . .	+ 5.7°	+ 2.6°	+ 1.1°	— 42°
Molecular weight found . .	213	217	215	—
Molecular refraction . .	67.39	67.91	65.88	67.48
Temperature at which mixture of 5.5 parts by volume of 60 per cent. (by weight) alcohol and one part by volume of oil becomes clear . .	5-6°	4°	12°	9°

The results of this important investigation are summarised as follows :—

(1) The so-called West Australian sandalwood oil is derived from a species of tree quite different from the *Santalum album*, Linn., the species from which the East Indian oil is obtained. It differs in general properties from the East Indian oil and, in order to avoid confusion, it should be given a name other than sandalwood oil.

(2) The oil, as distilled direct from the wood, differs in most of its analytical data from the genuine sandalwood oil. It does not fall within the limits allowed by the British Pharmacopœia as regards specific gravity, optical rotation, alcohol content, or solubility in 70 per cent. (by volume) alcohol at 20°.

(3) By fractional distillation and removal of the lower boiling sesquiterpene fraction it is possible to obtain an oil which passes the B.P. tests for genuine sandalwood oil, with the exception of the optical rotation, which is always well below the standard required by the B.P.

(4) Although it is easy by fractional distillation to obtain an oil containing more than 90 per cent. of alcohols (calculated as  $C_{15}H_{24}O$ ), nevertheless the alcohols present are not identical with

either of the two santalols present in East Indian oil, but are isomeric with them.

(5) There appear to be at least two alcohols present in the West Australian oil. They are probably to be represented as  $C_{15}H_{24}O$ , and, in order to distinguish them from the isomeric santalols, they have been termed  $\alpha$ - and  $\beta$ -fusanols.

(6) These fusanols yield hydrogen phthalates and phenyl-urethanes. The fact that they react much more slowly than the santalols with phthalic anhydride indicates that they are probably secondary, and not primary, alcohols.

(7) From their molecular refractions it is probable that both fusanols are bicyclic compounds containing two olefine linkings.

(8) The statement that during distillation of the oil under reduced pressure there is a loss of alcohols has not been confirmed; neither steam distillation nor distillation under reduced pressure appears to change the alcohol content.

(9) It is generally agreed that for perfumery purposes the West Australian oil is inferior to genuine sandalwood oil.

The writer (E. J. P.) does not agree with conclusion No. 3. Fractionation usually results in oils with a specific gravity below that of the true sandalwood oil, but the correct optical rotation can be attained.

**GALANGAL OIL.**—Galangal oil is used as a flavouring material rather than as a perfume. It is obtained by the distillation of the rhizome of *Alpinia officinarum*, a plant cultivated in China and Siam. The oil has a specific gravity 0.910 to 0.928, optical rotation,  $-1^{\circ}$  to  $-8^{\circ}$ ; and refractive index from 1.4760 to 1.4850. It contains terpenes, cineol, and oxygenated constituents not yet identified.

**GALBANUM.**—This body is a gum-resin obtained from several species of *Peucedanum*, principally *Peucedanum galbaniflorum*, belonging to the natural order *Umbelliferae*. It contains from 8 to 10 per cent., sometimes as much as 24 per cent., of essential oil of sharp aromatic odour. It is used to a small extent as an odorous fixative. The essential oil has the following characters:—

Specific gravity	.	.	.	0.905–0.955
Optical rotation	.	.	.	$-10^{\circ}$ to $+20^{\circ}$
Refractive index	.	.	.	1.4840–1.4960

It contains pinene, myrcene, a sesquiterpene (cadinene?), and

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a sesquiterpene alcohol,  $C_{15}H_{26}O$ , which has been termed cadinol. Five samples of the gum resin itself examined by Beckurts and Bruche had the following characters :—

Specific gravity . . . . .	1.11	1.13	1.109	1.133	1.121
Ash, per cent. . . . .	4.0	8.7	4.1	8.4	4.9
Resin, per cent. . . . .	63	56	58	54	60
Acid value of resin . . . .	22	19	40	19	25
Ester value of resin . . . .	82	91	69	63	90

**GARDENIA.**—The gardenia is a highly odorous flower, several species of which are cultivated, and whose perfume is highly esteemed. The perfume is rarely extracted from the flower, most of the bouquets known by the name being entirely artificial productions. The most common of the plants cultivated is *Gardenia florida*, also known as Cape jessamine ; *Gardenia grandiflora* is another well-known plant. They belong to the natural order *Rubiaceæ*. The plants are indigenous to tropical Asia and Africa, and also the Cape of Good Hope. In Bengal the plant is known as *Gundhuraja* : and in China, where its flowers are used for the perfuming of tea, it is called *Pak-sema-hwa*. The flowers from mixed cultivated species yield, on maceration with hydrocarbon oil and distillation of the extract, 0.0704 per cent. of an essential oil of specific gravity 1.009, and optical rotation  $+1.47^{\circ}$ . At 760 mm. pressure it commences to distil at  $204^{\circ}$  with partial decomposition. According to Parone (*Boll. Chim. Farm.*, 1902, 41, 489), it contains benzyl acetate, the acetic ester of methyl-phenyl-carbinol, linalyl acetate, methyl anthranilate, and terpineol.

The artificial perfume is built up on this composition, with the addition of various other synthetics, such as benzyl acetate, phenyl-ethyl aldehyde, and geraniol and its esters. (See also "Phenyl-ethyl Alcohol" and "Gardeniol.")

**GARDENIOL.**—This is a fancy name given to the acetic ester of phenyl-methyl carbinol, an isomer of phenyl-ethyl alcohol. (See "Phenyl-ethyl Alcohol" and "Gardenia.")

**GAULTHERIA OIL.**—See "Birch (Sweet), Oil of."

**GENET.**—See under "Broom."

**GERANALDEHYDE.**—This is an alternative name for the aldehyde citral  $C_{10}H_{16}O$  (*q.v.*).



**GERANIOL.**—Geraniol is one of the very important substances in the perfume industry. It is found in numerous essential oils, both in the form of esters, of which the principal is geranyl acetate (*q.v.*), and in the free state. For example, palmarosa oil contains 80 per cent. or more of free geraniol; citronella oil contains a considerable amount; all forms of geranium oil contain much geraniol in the form of esters, and a certain amount in the free state; and it is an important constituent of otto of rose.

Geraniol is not manufactured synthetically, but is extracted without any great trouble from oils which are rich in it, so that it is a regular commercial article, and is used to a large extent in the compounding of artificial perfumes.

Geraniol is a colourless, sweet smelling oil, having a rose-like odour. Its formula is  $C_{10}H_{17}OH$ , so that it is isomeric with nerol and with linalol. Its characters are as follows:—

Specific gravity . . .	0.880–0.883
Optical rotation . . .	0°
Refractive index . . .	1.4766–1.4786
Boiling point. . . .	228°–230°

It can be separated from those oils which contain an appreciable amount of it, by first concentrating it in the appropriate fraction under reduced pressure, and then mixing the fraction intimately with an equal weight of absolutely dry powdered calcium chloride, and allowing the mixture to stand in a desiccator for sixteen hours at a temperature of about  $-5^{\circ}$ . The pasty mass is then rubbed down with dry petroleum ether, and the liquid portion removed from the solid portion by means of a suction filter. After washing with more petroleum ether, the solid compound of geraniol with calcium chloride is treated with water, which decomposes the compound, with the liberation of the geraniol, and the oil is purified by fractional distillation. The geraniol distils over at  $228^{\circ}$  to  $230^{\circ}$ . To prepare it in a state of absolute purity it should be treated with sodium, and then dry ether and phthalic anhydride added. The geraniol sodium phthalate is hydrolysed by alcoholic solution of caustic potash, and the pure geraniol precipitated by the addition of water.

Flatau and Labbé effect the separation of geraniol and citronellol, which often occur together, in the following manner. The oil, first saponified, in order to decompose esters present, is fractionally distilled *in vacuo*. The fraction distilling at  $120^{\circ}$  to  $140^{\circ}$  at 30 mm. pressure, is heated with its own weight of phthalic

anhydride and its own volume of benzene. The mixture is dissolved in a solution of sodium carbonate, the solution extracted with ether, and the acid phthalic esters of geraniol and citronellol liberated by the addition of hydrochloric acid. These esters are dissolved in petroleum ether, and the solution cooled to  $-5^{\circ}$ . Under these conditions, the acid ester of geraniol separates out in the crystalline condition, whilst that of citronellol remains in solution. The esters, on saponification, yield the corresponding alcohols in a state of comparative purity. The geraniol ester melts at about  $47^{\circ}$ , and forms a silver salt which melts at about  $139^{\circ}$ .

Geraniol is characterised by its yielding a compound with calcium chloride, as above described, and by the formation of a phenylurethane melting at  $82^{\circ}$ . On oxidation geraniol is converted into its aldehyde, citral (*q.v.*).

Semmler and Schossberger (*Berichte*, 44, 991) have prepared an isomeric geraniol, which they have named isogeraniol. Geraniol can be, as just mentioned, oxidised to citral. If citral be heated with acetic anhydride, an alteration in its constitution takes place by the migration of a  $\text{CH}_2$  group. The citral is "*enolised*." The resulting *enol*-citral is reduced by means of sodium amalgam and alcohol, when the isomeric alcohol is obtained. Isogeraniol is an oil having a pleasant odour of roses, and possesses the following characters :—

Boiling point at 9 mm. . . . .	102°–103°
Specific gravity at 20° . . . . .	0.8787
Refractive index . . . . .	1.4732

For the estimation of geraniol, see under "Alcohols, Determination of."

The following method for obtaining geraniol commercially is given by Lewinsohn (*P. & E. O. R.*, 1924, 282):—

Java citronella oil is worked up chiefly for its geraniol, but this can only be produced economically if the citronellal obtained at the same time is further worked up for *d*-citronellol. It is, moreover, advantageous to separate from the residues the sesquiterpene compounds they contain, as they have very valuable fixative properties and find application in numerous compositions.

Thirty kilos of Java citronella oil are placed in a copper distillation vessel, to which is attached a copper fractionating column about 6 cm. in diameter and 120 to 140 cm. high, filled with glass

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beads or, better, with Rascheg rings, the vessel being heated by direct gas flame. The exit-tube of the column is connected with a copper spiral immersed in an iron tank of cold water and leading to a large vacuum flask which serves as a receiver. A stop-cock between condenser and receiver enables the latter to be changed while maintaining the vacuum in the distillation vessel. It is useful also to modify this arrangement, so that two receivers can be employed.

For the first distillation of the oil a not too high vacuum—say, about 10 mm.—is most suitable. The “crude first runnings” are the liquid distilling below  $95^{\circ}$  at 10 mm., thus ensuring the absence in the next fraction of anything boiling below the boiling point of citronellal. The second fraction, from  $95^{\circ}$  to  $110^{\circ}$ , is called “crude citronellal.” These two fractions must be distilled slowly to avoid overheating, but after  $111^{\circ}$  distillation may take place more rapidly, since only little citronellal will appear in the “crude geraniol” now collected. The heating is discontinued at  $130^{\circ}$ , and the residue in the distillation vessel is transferred to an enamelled container, where the residues from several operations are later worked up for sesquiterpene alcohols.

All three distillates are now redistilled separately, the “crude first-running” at 10 mm., the other two fractions at 3 mm.

The first fraction is distilled up to  $99^{\circ}$  at 10 mm., and the residue, consisting mainly of citronellal, is added to the “crude citronellal.”

The second fraction is distilled up to  $105^{\circ}$  at 3 mm., and the residue is added to the “crude geraniol.”

In this way are obtained a “final first-runings” (about 5 per cent. of the citronella oil used), and 50 to 52 per cent. of “technical citronellal,” which contains about 75 per cent. of pure citronellal, and is worked up for “*d*-citronellol.”

By the redistillation of the third fraction (“crude geraniol”) there is first obtained a little citronellal, which is added directly to the “technical citronellal.” The main fraction, namely, “technical geraniol,” comes over at  $115^{\circ}$  to  $120^{\circ}$  at 3 mm. The residue is added to the contents of the enamelled container.

In order to convert “technical geraniol” into “pure geraniol” it is necessary to remove completely the small traces of citronellal which spoil its odour. This is done by boiling for several hours with dilute caustic soda, whereby the aldehyde citronellal is resinified and remains in the residues on subsequent rectification.

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The operation is best performed in a double-walled iron vessel fitted with a good reflux condenser. After boiling for four hours, the mixture is diluted with cold water and the upper oily layer is separated from the lower aqueous layer. The oil is washed twice with lukewarm water, then with 50 per cent. acetic acid until just acid, next with sodium bicarbonate solution until again alkaline, and finally once more with water.

The oil is now distilled *in vacuo* from a 5-litre glass flask in an oil bath (or, for larger quantities, from a copper vessel). Pure geraniol comes over at 115° to 118° at 3 mm. as a water-clear liquid. The yield is 95 per cent. of the "technical geraniol."

**GERANIUM, OILS OF.**—The true geranium oil must not be confused with the so-called Indian (or Turkish) geranium oil. The latter is actually the East Indian palmarosa oil, an oil distilled from a member of the natural order *Gramineæ* (see under "Gingergrass Oil"), whilst true geranium oil is the product of various species of pelargonium belonging to the natural order *Geraniaceæ*. The principal species distilled are *Pelargonium odoratissimum*, *P. capitatum*, *P. graveolens*, and varieties of *P. Radula*, together with, in all probability, numerous hybrid forms. According to E. M. Holmes (*P. & E. O. R.*, 1913, 239), the majority of the species of pelargonium are natives of the dry rocky slopes of South Africa, but in their natural surroundings they are somewhat stunted in growth. When plantations are laid out in the south of Europe or in Algeria, etc., they are generally established on low-lying ground kept moist by a system of irrigation, so that the plants grow luxuriously after attaining a height of 2 feet 6 inches to 4 feet, with stems nearly an inch in diameter. The result is that three crops of leaves can usually be distilled annually when the growth is luxurious—as it is, for example, in Algeria. This, however, is not the case in the south of France. A considerable proportion of the geranium oil of commerce is distilled in the island of Réunion, and is known as Bourbon geranium oil; a large amount is also distilled in Algeria, and a certain amount is produced in Spain, Italy and Corsica. According to Holmes (*loc. cit.*) the plant used at Grasse, so far as can be judged from the leaf of the plant, appears to be *Pelargonium capitatum*. The plant cultivated in Bourbon is generally stated to be the same species, but the Bourbon-distilled oil more nearly corresponds in odour with that of the allied species *Pelargonium graveolens*.

In Grasse the plants are propagated by means of cuttings, set

out in October in sheltered beds, protected in frosty weather by means of straw mats. The cuttings are taken from the nurseries in April and planted out in open fields, where, under very favourable conditions, they will grow to 4 feet in height. In the neighbourhood of Nice they flower in August, but in cooler districts, such as Grasse, in October. The time of cutting in Algeria lasts from early spring until mid-autumn. In Bourbon the cutting proceeds during nearly the whole year. It has been found that the best yield of essential oil is obtained after a few days' rain, and when the leaves are gathered in the early morning before the buds have opened. The first crop in Bourbon is taken in April, the second in June, and the third in October. The plants require careful handling, as when the leaves are crushed there is always a loss of essential oil. In Réunion, as well as in Algeria, every geranium farm of any importance possesses its own still. In most cases care is taken to employ a form of still with a double bottom so that the leaves are not burned.

According to Cordemoy (*Rev. cultures coloniales*, 1904, 14, 170), the species cultivated in Réunion is *Pelargonium capitatum* (but see above). The plant flourishes best here at altitudes between 400 and 1,200 metres, the higher regions being too cold in the winter time. There are between 250 and 300 distillers of the oil in the island. About 700 to 1,000 kg. of geranium leaves are necessary to yield 1 kg. of oil.

In Corsica an excellent oil is produced on a small scale, *Pelargonium odoratissimum* being the principal species used. A few modern steam stills have been installed, and if modern methods are applied and transport difficulties are overcome (and these are very serious in Corsica), there is undoubtedly a big future for geranium distillation. As much as 1,300 kg. has been distilled in Corsica in a year, but this is considerably above the average.

Spain produces from 500 to 1,000 kg. of geranium oil in Valencia and Andalusia.

According to Ducellier ("Le géranium rosat. sa culture en Algeria," 1913, Algeria) there are about 2,200 acres in Algeria planted with geranium. There are plantations at Rovigo, Chelbi, Boufarik, Borurian, Mouzaïaville, Morocos, S. Faoueli, and other places. According to this authority, only *Pelargonium graveolens* is cultivated for distillation, and he considers, on the authority of Knutt, that *Pelargonium capitatum* is a hybrid of that plant. Whilst the Algerian geranium is propagated by cuttings, it is not

necessary to renew the plantations every year as is done in the south of France, as the Algerian winter is not severe enough to kill the plants. In some districts they will live for ten to twelve years. In Algeria, as in Spain and Réunion, three crops of leaves are gathered annually—one in early spring, a second in June, and a third in October.

The cultivation of the geranium plant is of paramount importance if a good yield of oil is to be obtained. This is especially true in the districts less favoured by natural conditions. Boutilly has clearly established the fact that superphosphate of lime is very favourable to high production of oil, and advises using this manure to the extent of about 800 lb. per acre. One of the most successful fertilisers for geranium plants is a mixture of sodium nitrate (200 parts), ammonium sulphate (150 parts), superphosphate of lime (300 parts), and potassium sulphate (150 parts). (See also *P. & E. O. R.*, 1913, 381, for cultural details.)

The leaves are the odour bearing portion of the plant, the flowers being practically odourless. Sometimes the oil is redistilled over rose petals, or rose petals are added to the geranium leaves when distilled. The resulting oil is, of course, of exquisite odour, and is sold as "oil of rose-geranium."

Charabot and Laloue have studied the development of the odorous constituents in the geranium. They found that these were entirely absent in the petioles and stems, and were only to be found in the leaves, where they appear to have their origin. The oil was distilled from the green plants in July, and again, from exactly similar plants, in August. These two distillates were found to have the following characters:—

	July.	August.
Specific gravity	0.897	0.899
Optical rotation	— 10°	— 10° 16'
Acid number	43.8	41
Esters	5.8 per cent.	10 per cent.
Free alcohols	64	62.1
Total alcohols	67.8	68.6

It was thus shown that (1) the acidity decreases as the plant matures, (2) the oil becomes richer in esters as growth proceeds, (3) the amount of total alcohols increases slightly and the amount of free alcohols decreases slightly as vegetation proceeds.

They also obtained interesting results in the examination of the oil separating from, and the oil dissolved in, the distillation waters

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of immature plants. These oils, and the two bulked, had the following characters :—

	Separated oil.	Soluble oil.	Total oil.
Specific gravity . . .	0.898	0.893	0.897
Optical rotation . . .	— 11°	— 5° 13'	— 10° 5'
Acid number . . .	47	16.5	42
Ester number . . .	16.6	6.7	15
Saponification number . . .	63.6	23.2	57
Total alcohols . . .	70.7 per cent.	77.5 per cent.	71.8 per cent.
Esters . . .	7.0 per cent.	2.8 per cent.	6.3 per cent.

According to Furukawa (*Jour. Chem. Ind. Tokio*, 1919, 22, 83), experimental cultivation of three species of geranium has been carried out on a farm near Tokio. These are *Pelargonium graveolens*, *P. radula*, and *P. denticulatum*. The oils distilled from the first two did not resemble geranium oil of commerce, whereas that from *P. denticulatum* resembled commercial geranium oil to some extent. The three oils had the following characters :—

	<i>P. graveolens</i> .	<i>P. radula</i> .	<i>P. denticulatum</i> .
Specific gravity . . .	0.9178	0.9234	0.886
Acid number . . .	183.6	5.6	7.17
Ester number . . .	4.8	31.7	12.8
Free alcohols . . .	22.1 per cent.	17.26 per cent.	60 per cent.
Total alcohols . . .	22    "	26.3    "	63.5 per cent.
Yield of oil . . .	1.75–2    "	1.5    "	5    "
Optical rotation . . .	+ 4° 6'	+ 3°    "	—

Puran Singh (*Indian Forest Records*, v., part viii., 1917, and *P. & E. O. R.*, 1917, 8, 327) has reported upon the wild geranium of the Nilghiris. He states that this plant is *Pelargonium graveolens* (*P. terebintaceum*, Harv. and Sond.). A yield of 0.044 per cent. of the weight of the entire plant was obtained, the essential oil having the following characters :—

Specific gravity at 16° . . .	0.888
Optical rotation . . .	— 5° 39'
Refractive index at 18° . . .	1.4600
Total geraniol . . .	74.8 per cent.
Free geraniol . . .	46.6    "
Esters as geranyl tiglate . . .	40.12    "

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The following values may be taken as covering practically all pure geranium oils from the sources named :—

	Bourbon.	African.
Specific gravity . . .	0.888–0.897	0.892–0.904
Optical rotation . . .	– 7° 50' to – 14°	– 6° 50' to – 12°
Refractive index . . .	1.4620–1.4685	1.4640–1.4720
Esters as geranyl tiglate .	22–33 per cent.	18–30 per cent.
Total alcohols as geraniol .	67–77 „	65–78 „

	French.	Spanish.
Specific gravity . . .	0.895–0.905	0.896–0.907
Optical rotation . . .	– 7° to – 11°	– 7° 20' to – 12°
Refractive index . . .	1.4630–1.4665	1.4640–1.4675
Esters as geranyl tiglate .	20–30 per cent.	26–42 per cent.
Total alcohols as geraniol	70–76 „	65–79 „

	Corsican.	Sicilian (?)
Specific gravity . . .	0.895–0.904	0.894–0.901
Optical rotation . . .	– 8° to – 11°	– 9° to – 11° 30'
Refractive index . . .	1.4640–1.4680	1.4645–1.4600
Esters as geranyl tiglate .	23–28 per cent.	26–35 per cent.
Total alcohols as geraniol .	68–75 „	65–77 „

The figures given above for Sicilian oil must be accepted with reserve. According to Pellini (*Ann. di Chim. Applic.*, vii., 3), *Pelargonium capitatum* is the only species found in Sicily, and the following figures were obtained for four samples of oil distilled from the earliest to the latest period of flowering :—

	1.	2.	3.	4.
Specific gravity . . .	0.915	0.899	0.909	0.902
Optical rotation . . .	– 5.40°	– 6.56°	– 6.14°	—
Refractive index at 25° .	1.4686	1.4647	1.4670	1.4653
Esters . . .	Per cent. 38.77	Per cent. 30.04	Per cent. 40.12	Per cent. 38.39
Total alcohols . . .	47.1	60.3	59.7	59



All geranium oils should be soluble in 3 volumes of 70 per cent. alcohol. The principal constituent of geranium oil is the alcohol geraniol  $C_{10}H_{18}O$ , in the free condition to the greater extent, and to a lesser extent in the form of esters, of which the tiglic acid ester is the principal. There is also present a notable amount of citronellol  $C_{10}H_{20}O$ , which, together with the geraniol and very small quantities of several other alcohols, makes up the "total alcohols as geraniol." The proportion of citronellol to geraniol varies in the different types of geranium oil. In Spanish oils the citronellol forms about 35 per cent. of the total alcohols, whilst in African oils only about 20 per cent. of the total is citronellol. In Bourbon oils the two alcohols are present in about equal proportions. Linalol, terpineol, menthol, phenyl-ethyl alcohol, and possibly borneol and amyl alcohol, are also present. Pinene, phellandrene, menthone, and citral are present, and traces of dimethyl sulphide (in Bourbon oils).

Geranium oil is largely used in perfumery, very large quantities being consumed in the manufacture of high-grade soap. The oil was at one time largely adulterated in a very crude fashion. To-day, owing to the ease with which the cruder adulterants are detected, adulteration is less common, and where it is practised it is on a more scientific basis. Palmarosa oil and artificial esters are sometimes used.

E. M. Holmes (*P. & E. O. R.*, 1913, 372) gives the following interesting list of hybrid pelargoniums (the majority of which have had their relationships indicated by Mr. J. Fraser, of Kew) as showing the extent to which the alteration in odour may go by hybridisation. The relationships of those marked with an asterisk are on the authority of Fraser; the remainder are classified by E. M. Holmes.

*Pelargonium adulterinum*

\*Lady Mary . . . . . Weak citronellal.

\*Duchess of Devonshire . . . . . Ladanum.

*P. angulosum* (+ *cucullatum*)

\*Pretty Polly . . . . . Faint rose, ladanum, and citronellal.

*P. blattarium* . . . . . Citronellal, slight ladanum.

*P. capitatum*

\*var. *conspicuum* . . . . . Faint rose, ladanum, and citronellal.

\*Dale Park Beauty . . . . . Rose, ladanum, faint butyric.

\*Kimberley . . . . . Ladanum and pepper.

\*Mrs. Kingsbury . . . . . Faint rose and ladanum.

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*Lucerne . . . .	Faint rose and tansy.
*Old Unique . . . .	Slight rose and strong ladanum.
Scillonian . . . .	Rose and citronellal.
*Shottenden Pet . . . .	Rose and faint peppermint.
<i>P. crispum</i> .	
var. <i>compactum</i> . . . .	Citronellal, faint rose.
Clyne's Seedling . . . .	Rose and citral.
<i>P. denticulatum</i> .	
*var. <i>filicifolium</i> . . . .	Faint butyric and ladanum.
Pheasant's Foot . . . .	Rose, ladanum and faint butyric.
<i>P. fragrans</i> . . . .	Faint rose and tansy.
<i>P. gratum</i> . . . .	Tansy and faint nutmeg.
<i>P. graveolens</i> . . . .	Citronellal.
*Little Gem . . . .	Faint rose, peppermint, ladanum.
*Monsieur Nonin . . . .	Ladanum, slightly butyric.
*Scarlet Pet . . . .	Ladanum.
*Westonbirt . . . .	Rose, citronellal, and ladanum.
<i>P. papilionaceum</i> . . . .	Citronellal, slightly mousy odour.
<i>P. pinnatum</i> . . . .	Rose, ladanum, and slightly butyric.
<i>P. quercifolium</i> .	
Curly . . . .	Ladanum, faint citronellal.
Agnes . . . .	Strong pepper.
Danesford . . . .	Ladanum and faint peppermint.
*Fair Ellen . . . .	Ladanum.
*Fair Emily . . . .	Faint citronellal, ladanum.
*Miss Dorrien Smith . . . .	Ladanum, faint rose.
Sweet Ellen . . . .	Slight citronellal, ladanum, pepper.
<i>P. quinquevulnera</i> . . . .	Citronellal.
<i>P. selectum</i> . . . .	Rose and citronellal.
<i>P. tomentosum</i> .	
*Godfrey's Bride . . . .	Peppermint and faint rose.
<i>P. vitifolium</i> .	
*Mrs. Babington . . . .	Weak rose.

**GERANYL ACETATE.**—This ester, of the formula  $C_{10}H_{17}.OOC.CH_3$ , is of very great importance to perfumers. It is a constituent of many essential oils, and is used on a considerable scale in the manufacture of numerous artificial perfumes, especially those which are required to have a rose effect. It is prepared artificially by heating geraniol and acetic anhydride in the presence of sodium acetate, washing the resulting oil with water, and finally rectifying under greatly reduced pressure. When pure, geranyl acetate has the following characters:—

Specific gravity at 0° . . . .	0.9388
Specific gravity at 15° . . . .	0.9174
Boiling point. . . . .	242°–245°
Refractive index . . . . .	1.4628 at 15°

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It is not easy on a commercial scale to manufacture this ester in a state of absolute purity, but good-quality samples as met with on the market should have an ester content of not less than 95 per cent., and should give figures approximating to the above. Geranyl acetate forms the principal constituent of the essential oil of *Eucalyptus Macarthurii* (q.v.), in which it occurs, to the extent of over 66 per cent., associated with about 10 per cent. of free geraniol.

**GERANYL BENZOATE.**—This ester,  $C_{10}H_{17}.COO.C_6H_5$ , is used to some extent in the compounding of artificial floral bouquets. It is prepared by mixing 3 kg. of geraniol with 1.5 kg. of pyridine, cooling to ice temperature, and adding, with constant agitation, 2.5 kg. of benzoyl chloride, avoiding any substantial rise in temperature. The mixture is allowed to stand for several hours at ordinary temperature, and the separated oil is washed, first with water and then with a dilute warm solution of sodium carbonate. The resulting oil contains unaltered geraniol, but it cannot be purified by rectification, as it is partially decomposed on distillation, even *in vacuo*. If, however, the product be washed with a 50 per cent. solution of sodium salicylate, the unaltered geraniol is dissolved out and the product becomes considerably richer in true geranyl benzoate. The pure ester boils at  $195^\circ$  at a pressure of 15 mm.

**GERANYL BUTYRATE.**—Geranyl butyrate  $C_{10}H_{17}.OOC(CH_2)_2.CH_3$  is an oil of sweet rose odour, finer than that of geranyl acetate, and of great value to the perfumer. It is prepared by heating geraniol dissolved in pyridine with butyryl chloride, and is an oil boiling at  $143^\circ$  at 13 mm. pressure. It is used to advantage in the preparation of artificial otto of rose and in many artificial floral perfumes. Its specific gravity is about 0.892, and refractive index 1.4550.

**GERANYL FORMATE.**—This ester,  $C_{10}H_{17}.OOC.H$ , is one of the most valuable of the geranyl esters to the perfumer. It has not been found in any essential oil, but may be prepared artificially by allowing formic acid to react in the cold with geraniol in the presence of a trace of sulphuric acid as a condensing agent. It has a fine rose odour, somewhat like that of the tea rose, or, perhaps, "green rose leaves." It is, when pure, an oil boiling at  $114^\circ$  at 15 mm. pressure; but it is impossible to manufacture it in a pure condition on the commercial scale, so that the commercial ester rarely contains more than 95 per cent. of actual ester.

A good-quality geranyl formate should have a sweet powerful odour, free from any trace of "acid" odour, and should have the following characters :—

Boiling point at 3 mm. . . .	88°
Specific gravity . . . . .	0.920-0.927
Optical rotation . . . . .	0°
Refractive index . . . . .	1.4640-1.4665
Actual ester . . . . .	at least 95 per cent.

**GERANYL ISOBUTYRATE.**—This ester,  $C_{16}H_{17}.OOC.(CH)(CH_3)_2$ , is isomeric with and similar in odour to geranyl butyrate. It is an oil which boils at 137° at 13 mm. pressure.

**GERANYL ISOVALERIANATE.**—This ester has the formula  $C_{11}H_{17}.OOC(C_4H_9)$ . It has a modified rose odour and is capable of imparting a very characteristic note to artificial rose perfumes. Its specific gravity is about 0.890, and refractive index 1.4570.

**GERANYL PROPIONATE.**—This ester, which is intermediate in character between the acetate and the butyrate, has a specific gravity about 0.9025, and a refractive index 1.4580.

**GERANYL TIGLATE.**—This ester,  $C_{10}H_{17}.OOC.C(CH_3)_2$ , is the characteristic odour bearer in geranium oil. In the determination of the esters in this oil they are always returned as geranyl tiglate, which requires a different calculation from that for linalyl acetate. Geranyl tiglate is a highly odorous oil with a sweet rose-geranium odour.

**GINGER.**—This highly aromatic substance finds its principal employment as a spice. The resinous matter and the high boiling constituents of its essential oil, however, have a high fixative value, and to a small extent it can be used to advantage in perfumery. Ginger of commerce is the dried rhizome of *Zingiber officinale*, probably a native of tropical Asia, which is largely cultivated in the East and West Indies, in China, in Africa (Sierra Leone), and to a small extent in Australasia. The method of cultivation in Jamaica, which produces the most esteemed ginger, is as follows (*Bull. Botanical Dept. of Jamaica*, December, 1891): "The most suitable soil for ginger culture is a well-drained clayey loam. The land should be well dug and cleared of weeds. Small pieces or protuberances of the root, 1 or 2 inches long, are planted during March or April, 4 inches deep and 9 to 12 inches apart. It is well to cover the land with a moulding of dead leaves, straw or litter, mixed with manure. In a few months the whole ground

will be covered. The flowers appear in September. When the stalks wither, in the following January or February, it is time to dig up the roots. When the tubers have arrived at maturity and have put forth stems, they are fibrous, but before this takes place they are still succulent, and, if required for preserving, should then be taken up. Ginger is an exhausting crop on the soil, and should not be planted on the same ground two consecutive years. The yield per acre is said to be 4,000 lb. and upwards."

Ginger rhizomes are sometimes imported in the soft juicy condition known as green ginger, but the ordinary gingers of commerce are washed, dried, and scraped (uncoated ginger), or are merely washed and dried (coated ginger). It is also sometimes bleached or coated with lime to erroneously suggest bleaching.

Sawer (*Odorographia*, ii., 95) gives the following account of the cultivation of ginger in India as carried on in the hill states adjoining the Ambalah district:—

"Ginger is principally produced in Mahur Massa, Patra, Darva, Kothi, Kotahi, Bagal, and Jayal. The best pieces of last year's harvest are selected and placed in the corner of a house in the month of Phagan; the heap is then smeared over and covered with cow dung to keep the roots from drying up in Har month, when the first rain falls. The land is ploughed up two or three times and then divided off into beds, with a little raised edge round each bed, care being taken to make openings to let superfluous water run off; for if water stands on the crop the roots will rot. Little pieces of the roots are then buried 3 inches deep in the soil at intervals of 9 inches, and the field is next covered over with the leaves of trees, which keep the soil moist, and over the leaves is spread manure to a depth of  $\frac{1}{2}$  inch. When it rains, the water, impregnated with manure, filters rapidly through the leaves to the roots. Artificial irrigation is not employed while the rainy season lasts, but from Assuh to Poh it is necessary. In the month of Poh the plants are about 2 feet high. In the months of Sawan, Bhadon, and Assuh the field is weeded three times."

According to Ridley ("Spices," Macmillan & Co., London, 1912), there do not seem to be many forms or varieties of the plant, as might be expected from the propagation being almost entirely by means of cuttings.

The Malays are acquainted with three forms, which they know under the following names:—

*Halyia betul* (true ginger) is the name given to a form with broad leaves and a very white-fleshed rhizome. It is taller than

the other varieties, and is used for making sweetmeats and as an ingredient in curries.

*Halyia bara* or *Halyia padi* (*bara* = hot coals ; *padi* = rice) is a smaller plant than the former, and is of greater pungency. It is used locally in medicine.

*Halyia hudang* is of a redder tint than the others, and is used in native medicines.

In Jamaica the planter divides the plant into "blue" ginger and "yellow" ginger, so called from the tint of the rhizome. Blue ginger is also known as "flint" ginger, and the yellow variety as "turmeric" ginger. According to Kilmer, the plants producing these varieties cannot be distinguished except by the tints of the rhizomes. He suggests that blue ginger is a degenerate form. The root of the blue ginger is hard and fibrous, and is of less value commercially than that of yellow ginger.

Canton ginger, which is known in this country in the form of preserved ginger, appears to be a more distinct variety. The rhizome is thick and succulent, hence its use as a sweetmeat. It is said that it cannot be dried in Canton on account of the absence of sufficient sun heat in the season when the rhizome is dug. There has been a good deal of confusion as to the plant from which the Chinese ginger is obtained. In 1891 plants stated to be the source of Canton ginger were sent to Kew Gardens, and were identified as *Alpinia galanga*, but it is now established that these were the wrong plants, and that Chinese ginger is actually the product of *Zingiber officinale*.

Ginger was, according to Ridley (*loc. cit.*), one of the earliest Oriental spices known to Europeans, and was certainly known to the Greeks and Romans. The name *zingiber* (ginger) is probably derived from the Sanskrit *sanjabib* through the Arabic *zanzabib*. The Greeks and Romans appear to have obtained it from the Arab traders in the East, who doubtless brought it from India. Its original home is not known, as no one seems to have met with it in a wild state. The spice was well known in England before the Norman Conquest, and in the thirteenth and fourteenth centuries was nearly as common in trade as pepper. One pound was, at this time, worth about as much as a sheep.

In the fourteenth century the Italians classified ginger in three forms :—

(a) *Baladi*, country or wild ginger.

(b) *Columbino*, that imported from Columbum (Quilon, in southern India).

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(c) *Mecchius*, that imported *viâ* Mecca.

Marco Polo is probably the first traveller who records having seen the plant alive (1280–1290). He met with it in China, Malabar, and Sumatra. It was described in 1292 by John of Montecorvino, and later by Nicolas Conti.

Preserved ginger in syrup, or green ginger, was imported into Europe as a sweetmeat as early as the Middle Ages. As the rhizomes of ginger are very easily transported in a living state for considerable distances, it is not surprising that the plant was introduced into America very soon after the discovery of the New World, and before any other Oriental spice. It was brought to New Spain (Mexico) by Francisco de Mendoza, and the rhizomes were exported from San Domingo as early as 1583, and from Barbados in 1694.

Ginger itself is not adulterated to any great extent, although from time to time ground ginger mixed with the powdered exhausted spice is found on the market, and sometimes samples are found with too much mineral matter.

Preparations in the liquid form, however, which, from their name, would appear to be made from ginger—such as essence of ginger, ginger ale, ginger beer, and similar preparations—are very frequently adulterated with capsicum, so that a fictitious strength is given to the preparation at a trifling cost.

A. H. Allen (*Analyst*, xix., 124) gives the following analyses for pure gingers :—

	A	B	C	D	E	F	G
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1. Total ash . . . . .	3.54	5.23	4.41	5.15	5.53	7.69	5.39
2. Ash soluble in water . . . . .	2.36	2.59	2.22	2.57	2.87	2.36	—
3. Alkalinity of 2 as K <sub>2</sub> O . . . . .	0.96	0.96	0.29	0.13	0.15	0.20	—
4. Extracted by 90 per cent. alcohol . . . . .	7.33	7.70	7.37	6.22	8.45	—	4.65
5. Extracted by proof spirit . . . . .	20.95	19.7	10.7	10.45	7.55	21.6	5.85
6. Extracted by cold water . . . . .	14.6	13.16	14.95	14.55	14.5	14.6	8.14
	H	I	J	K	L	M	—
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
1. Total Ash . . . . .	3.61	3.19	2.72	3.52	3.29	4.5	—
2. Ash soluble in water . . . . .	1.24	1.45	0.69	1.11	0.97	1.37	—
3. Alkalinity of 2 as K <sub>2</sub> O . . . . .	0.27	0.20	0.23	0.23	—	—	—
4. Extracted by 90 per cent. alcohol . . . . .	7.09	—	6.88	7.86	—	—	—
5. Extracted by proof spirit . . . . .	13.0	16.1	11.8	12.4	—	—	—
6. Extracted by cold water . . . . .	8.33	9.8	8.5	7.2	8.1	7.4	—

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The following analyses are due to Richardson :—

Sample.	Molsture.	Ash.	Essential oil.	Fixed oil and Resin.	Starch.	Fibre.	Nitrogen.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
1. Calcutta . . .	9.6	7.02	2.27	4.58	49.3	7.45	1.01
2. Cochin. . . .	9.41	3.39	1.84	4.07	53.3	2.05	1.12
3. Unbleached Jamaica	10.49	3.44	2.03	2.29	50.6	4.74	1.74
4. Bleached Janfaica .	11.0	4.54	1.89	3.04	49.3	1.70	1.48
5. Bleached Jamaica .	10.11	5.58	2.54	2.69	50.7	7.65	1.46

For the detection of capsicum in preparations of ginger, Garnett, Grier, and La Wall (*Analyst*, xxxiv., 321) recommend the following method. The liquid, such as ginger ale, is warmed to expel CO<sub>2</sub> and alcohol, if present. The aqueous residue is rendered acid with dilute sulphuric acid and shaken with 50 c.c. of ether for a minute. If the residue from the ether, which is allowed to evaporate spontaneously, weighs less than 10 mg., it is treated with 2 c.c. of  $\frac{N}{2}$  alcoholic caustic potash solution. An additional 1 c.c. of the alkaline solution is added for each further 10 mg. of residue. The mixture is gently heated to boiling on a water bath for thirty minutes under a reflux condenser. The alcohol is then poured off, water added, and the liquid well shaken with ether. The ether is separated and evaporated. If the residue has a hot pungent taste, capsicum is present. One part of capsicum in 10,000 parts of liquid can thus be detected.

The essential oil distilled from the true ginger rhizome has a highly aromatic odour, but is free from the pungent flavour of the spice, which resides in its resinous constituents. The rhizome yields from 2 to 3 per cent. of a greenish-yellow oil having the following characters :—

Specific gravity . . . . .	0.874–0.886
Optical rotation . . . . .	— 25° to — 50°
Refractive index . . . . .	1.4885–1.4950
Acid value . . . . .	0–2
Ester value . . . . .	1–15
Ester value after acetylation . . . . .	30–45

Oils will be found, however, from time to time whose characters fall outside the above limits. Bacon, for example (*Philippine Jour. Sci.*, 1910, 5, 259), examined a sample distilled in the Philippines which had an optical rotation + 5.9°. Japanese oil has been found having a specific gravity 0.894, and optical



rotation  $+ 9^{\circ} 40'$ . A Java oil has been found with an optical rotation  $+ 13^{\circ} 9'$ .

The oil consists principally of the terpenes *d*-camphene and  $\beta$ -phellandrene, with a sesquiterpene (or mixture of sesquiterpenes) known as zingiberene. Cineol, citral, borneol, methyl-heptenone, nonyl aldehyde, linalol, a sesquiterpene alcohol named zingiberol,  $C_{15}H_{26}O$ , and various esters have been detected in the oil. The principal odour bearer is probably zingiberol.

**GINGERGRASS OIL.**—This useful perfume oil is conveniently considered in conjunction with palmarosa oil, the so-called East Indian geranium oil. (See "Geranium Oils.") Considerable mystery has for many years surrounded these two oils, and the questions involved cannot yet be regarded as solved. So late as 1893 the authors of "Pharmacographia Indica" stated of the oil distilled from *Andropogon Schœnanthus* (which, however, is to-day renamed *Cymbopogon Martini*), that: "The oil distillers in Khandesh call the grass *Motiya* when the inflorescence is young and of a bluish-white colour; after it has ripened and become red, it is called *Sonfiya*. The oil obtained from it in the first condition has a more delicate odour than that obtained from the ripened grass. The motiya oil is usually mixed with the second kind, which, by itself, would not fetch a good price in the European market. (This may to a great extent account for the considerable difference in the quality of the two commercial grass oils, the so-called geranium oil and ginger grass oil)."

For many years gingergrass was regarded on the London market as merely adulterated palmarosa oil. It appears certain, however, that the two oils are two quite different pure oils, and that the statement quoted above from the "Pharmacographia Indica" is incorrect. The grass *Cymbopogon Martini* exists in two forms, whose botanical differences have not been made out. The native name for the grass is *Rosha* or *Rusa* grass, and the two forms are known as *Motia* and *Sofia*. The motia grass yields palmarosa or Indian geranium oil, whilst the sofia grass yields gingergrass oil.

The grass grows, according to Dr. Dymock, freely, though not very widely, on open hill sides in West Khandesh, especially in Akrani. According to a report by R. S. Pearson (*Indian Forest Records*, vol. v., part vii.) the most important localities from which Rosha oil is obtained in the Bombay Presidency are, North, East, and West Khandesh, and the North and South Nasik Divisions of the Central Circle, and to a less extent from the Surat Dangs and Panch Mahals Divisions of the Northern Circle. In these

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localities the bulk of the grass comes from the Shahada, Taloda, Pimpalner, and Akrani Ranges of Khandesh, while the Central and Northern Ranges of the North Nasik Division also produce considerable quantities.

According to a report received from Messrs. Volkhart Brothers, Ltd., Khandesh and Nasik were formerly the chief exporting

Name of Circle.	Name of Division.	Approximate area for which leases are given for the collection of Rosha grass.	Remarks.
Berar	Melghat	<div style="display: flex; justify-content: space-between;"> <div> Open forests A.  Dense forest B.    Total </div> <div style="text-align: right;"> Acres.  220,513  522,459  <hr/> 742,972 </div> </div>	Generally the "Motia" grass is found in class A and the "Sofia" in class B forests.
"	Nimar	No information available, though the area is known to be large.	
"	Betul	86,930	
"	Buldana	33,430	In the Yeotmal Pusad Taluqa.
"	Akola	4,788	In the Narnala block.
"	Amraoti	31,199	In the Morsi-Warud and Amraoti Ranges.
Northern	Chhindwara	Reserved forest { 40,000 20,000	In the Ambara Range.
"	Saugor	. . . . .	In Ryotwari and Malguzari lands.
"	Mandla	. . . . .	Small quantities only available.
Southern	Balahgat	. . . . .	Area not known.
			Only a very small quantity of "Sofia" grass available. In other parts of this Circle the grass is not available in commercial quantities.

districts in India, but now they are of less importance than the Berars.

The most important areas from which Rosha grass is obtained in the Central Provinces are in the Melghat, Betul, and Nimar Forest Divisions of the Berar Circle. The grass is found elsewhere, scattered in small quantities through the forest, and though distilled in some divisions it is not worked on an extensive scale.

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The table on p. 268 gives the approximate areas in each division in which leases are annually given for the collection of Rosha grass.

The most important areas from which Rosha grass is obtained in Central India are the Ali Rajpur, Jhabua, Dhar, and Barwani States, of which the Jhabua State is the most important. In Ali Rajpur, Rosha grass is found growing in the southern and western parts of the State and nearly all over the Jhabua State, while in Dhar it is found in limited quantities in the Mandu, Dharanpuri, Kukshi, and Nananpur Ranges. In Barwani State, Rosha grass is found in large quantities in the Narbadda and Pati Ranges, and in limited quantities in the Silawad, Pansemal and Rajpur Ranges.

The areas over which Rosha grass is found growing in Ali Rajpur, Jhabua, and Dhar States is not known, while that in the Barwani State is given by the local authorities to be as follows :—

Name of State.	Name of Range.	Approximate area for which leases are given for the collection of Rosha grass, in acres.	Average No. of tons of grass extracted.	Remarks.
Barwani	{ Narbadda Range	48,870	} 45 {	{ These two Ranges are leased together. In 1909-10 no grass was available. In 1911-12 and 1912-13 no grass was available.
	{ Pati Range .	87,080		
	{ Silawad Range .	34,905		
	{ Pansemal .	34,301		
	{ Rajpur Range .	3,745		

A certain amount is also available for distillation in Madras.

Pearson (*loc. cit.*) states that the local practice, which is the only method used at present for extracting the oil, is by direct fire-heated stills, steam stills having been used only experimentally. The flower and leaf, and small portions of the stem are used for distillation. The flower and the upper third of the stem are collected in September and October, being tied into bundles or "pulas" of about 4 oz. each. A second cutting is frequently made when the grass flowers for its second time. The grass is either distilled in a partially green state, or the flower heads and portions of stem are carefully dried in the shade before distilla-

tion, during which process they lose from 20 to 40 per cent. of their weight. The plant used by the local distillers varies but little from district to district, being always of a primitive type. The still is always erected quite close to a stream or pond, so as to provide plenty of water for condensation purposes. The still itself is of iron or copper, and is cylindrical in shape, having a large opening at the top for the introduction of the charge. The stills hold from 12 to 14 gallons, and are charged with 1 part of grass and 4 parts of water, and then heated over a naked fire. Experiments carried out by Messrs. Pheroze & Co., of Bombay, resulted in a yield of 0.87 per cent. of oil by distilling the entire plant, which consisted of 54 per cent. of stalks, 28.5 per cent. of leaves, and 17.5 per cent. of flower tops. When these portions of the plant were distilled separately, the following yields of oil were obtained: stalks, 0.04 per cent.; leaves, 1.32 per cent.; flower tops, 1.71 per cent. The yield, however, is variable, and may reach 1 per cent. on the fresh plant, and nearly 2 per cent. on the dried plant.

The industry is a very important one, the annual distillation reaching from 80,000 to 120,000 lb., possibly even more.

Messrs. Volkart Brothers state that Rosha oil, both "Motia" and "Sofia," is consumed all over India for the manufacture of native "attars." Calcutta, Benares, and other places in northern India take as much as 3,000 to 5,000 lb. annually for this purpose, the oil first finding its way to Bombay, from which place it is sent to the north. In addition to the above quantity, 3,000 to 4,000 lb. of this oil finds its way direct to Burhanpur in the Nimar district, where it is made up locally into "attars." Probably small quantities are also retained in the producing districts and manipulated locally, but on this point no reliable information is available.

A. D. Bhote, a Range Forest officer in the Central Provinces, states that Rosha oil, and especially "Motia," is considered to be a good remedy for rheumatism and is sold for this purpose in most Indian bazaars. It is also used to a limited extent for scenting soap. The oil is considered to be a cooling astringent and is used in the case of headaches, for skin diseases, and is said to be a cure for baldness; it is never taken internally, however, except in very small doses as a cure for bilious complaints.

Its chief use in India is for adulterating "attar" of roses, either by dilution of the "attar" or by sprinkling the rose leaves with Rosha oil before distillation takes place. Bhote states that

before using Rosha oil to adulterate rose "attar" it has to be refined; this is done by shaking the Rosha oil with water mixed with lime juice and then exposing it to the rays of the sun. This is no doubt done to bleach the colour of the oil in order to make it resemble "attar" of roses in colour. Further, he states that Rosha oil which in the process of manufacture has been overheated is too dark in colour for use in adulterating rose "attars."

Rosha oil, as found on the market in India, is rarely absolutely pure; in fact it is nearly always heavily adulterated with turpentine, linseed, rape, ground-nut oils, etc., the adulteration being often carried out by the distillers themselves. On re-distillation to obtain pure oil, a more concentrated and more strongly perfumed oil is obtained, which is, however, not often found on the Indian market.

R. S. Pearson (*loc. cit.*) has made the following suggestions for improving the industry, and, considering that these two important oils are practically a monopoly of India, it is to be hoped that his suggestions will be acted upon:—

It requires no very deep knowledge of the Rosha grass industry to arrive at the conclusion that the business is not being carried on to the best advantage of everybody concerned. Everything points to the desirability of introducing steam-distillation plants, not only in order to obtain a greater quantity of oil from a given quantity of grass, but to reduce the cost of production by a saving in fuel and labour.

After carrying out experiments with the steam-distillation plant in the Melghat Division, the following conclusions have been arrived at:—

(1) That approximately 20 per cent. more oil can be obtained from a steam plant than from a direct-fire still when using thoroughly sun-dried grass. Again, when using steam distillation with dry and green grass, 100 per cent. more oil was obtained from the latter for the reason that the oil has not time to volatilise out of the green grass. The above are the two extremes, so that were a plant erected of sufficient size to work off the grass nearly as quickly as it came in, namely, in a partially green state, the yield, when using a steam plant, would be at least 50 per cent. greater than from the direct-fire still at present in use.

(2) That the consumption of fuel when using a boiler is somewhere about 100 per cent. less than that required for a direct-fire still, and 80 per cent. less than that required when using a modified direct-fire still.

(3) That the amount of labour required to work a steam still is, if anything, less than that required for a direct-fire plant, though the actual pay of a boiler man, working also as an overseer, is somewhat greater than that of an overseer necessary to supervise the plant at present in use.

(4) That the rate of distillation in all three types of stills is about the same, though the time taken to charge and unload a steam or modified direct-fire still is less than that required for a direct-fire still.

(5) That better results are obtained when working at 10 lb. pressure in the boiler than at higher pressures.

(6) At present no redistillation is carried out, the colour of the oil being pale yellow, which on storage becomes darker, due to oxidation. When distilling with either a direct-fire or steam still, traces of moisture become emulsified with the oil, more so in the latter case. To overcome this difficulty a simple anhydrous sodium sulphate filter is recommended.

(7) It should be remembered that the rectified oil is water white; this can only be obtained by redistillation, which can only be done by adopting the steam process. Whether redistillation will pay depends entirely on the fluctuation of prices in the market. It is a point that should be carefully borne in mind as the industry expands.

(8) That where at present only one small still is worked in any one locality—in other words, where only small quantities of Rosha grass are available—it would not be worth while erecting a steam plant, but that far better results than those given by a direct-fire still would be obtained by using a modified direct-fire still fitted with a false bottom, so that the water and grass should not come in contact, thus introducing steam distillation on a modified scale, as advocated by Dunbar Brander. Where, however, two small stills are at present worked a small portable steam plant is advocated, which could be moved at least once in the working season to another place after the grass in the first locality had been exhausted. The third case to be considered deals with such places as exist at the foot of the hills in the Melghat, where, year after year, three or more Rosha stills are erected in one place and where the grass is abundant. In such localities it would be advisable to erect more permanent plants, consisting of an 8-h.p. boiler, four or more stills, and one condenser to every two stills, the whole covered in by a roof for the protection of the plant during the monsoon months.

(9) That the yield of oil when using a steam plant or a modified direct-fire still varies little when using sun-dried grass, and that the chief advantage in a steam plant is economy of fuel and facility in regulating the duration and rate of distillation.

The characters of the Motia oil, or palmarosa oil, are very admirably summarised by Puran Singh, Chemical Adviser to the Forest Research Institute, Dehra Dun (*Indian Forest Records*, vol. v., part viii., p. 46) as follows :—

The constants of the "Motia" oil have been determined by various chemists from time to time, but it has always been doubtful how far the samples examined could be regarded as genuine. Besides, it is not known if the oil obtained by a modern steam-distillation plant and subsequently refined has been put on the market, and if its constants have been recorded. Through the courtesy of Mr. C. E. C. Cox, officiating Forest Economist, Forest Research Institute, Dehra Dun, the writer had the opportunity of examining crude oils obtained by steam distillation by Mr. R. S. Pearson, and it may not be without interest to give the constants of the oils as obtained in the laboratory of the Forest Research Institute, Dehra Dun.

As regards the constants of the "Motia" oil recorded till now, Parry (*"Chemistry of Essential Oils, etc.,"* 2nd ed., p. 182) gives a very accurate summary: "When pure the oil has a specific gravity of from 0.885 to 0.896, and is almost inactive optically, rotating from  $-2^{\circ}$  to  $+2^{\circ}$ , usually under  $1^{\circ}$  either way, and rarely up to  $+4^{\circ}$ . (Gildmeister and Hoffman, in their *"Volatile Oils,"* last edition, record a maximum of  $+6^{\circ}$ .) The oil should dissolve in three times its volume of 70 per cent. alcohol. Its refractive index is about 1.4800. . . . The esters do not require less than 3 nor more than 5 per cent. of potash for saponification. The usual amount of esters present is from 10 to 15 per cent. The free geraniol varies from 65 to 85 per cent. The total geraniol, free and combined, varies from 72 to 92 per cent."

Some time ago Mr. Burkhill, the then officiating Reporter on Economic Products to the Government of India, sent a number of specimens of "Motia" oil collected by himself from the Indian distillers to Messrs. Schimmel & Co., Leipzig. In their *Semi-Annual Report* for 1910 Messrs. Schimmel & Co. published the constants given in the table on p. 274 for these oils.

Even these samples were not of the very best quality that it is possible to distil from the grass. The crude water-distillation method as employed by Indian distillers is likely to affect the

quality of the oil injuriously. The water-distilled oil as put on the market is, as far as it is known, never rectified, though Parry mentions having met with rectified water-white Motia oil. In this connection it may be remarked here that, according to the *Reports of Messrs. Schimmel & Co.*, this valuable Indian product is losing its reputation in Europe owing to lack of uniformity in the quality of the oil and to the prohibitive prices asked for it. Both of these complaints can be easily removed, the first by rectification of the oil, and the second by better methods of distillation. At present, in small crude stills, the Indian distillers cannot handle sufficiently large quantities of the fresh green grass in the proper season, nor can they arrange to dry and store up the grass for future use. By proper organisation and by improving the distillation plant it is possible to increase the annual Indian

No.	Place of production.	d. 15°	$\alpha$ D	ND 20°	Acid No.	Ester No.	Total gera- niol.	Solubi- lity in 70 per cent. alcohol.
<i>Palmarosa oils (Motia oils).</i>								
1	Chitar .	0.8904	+ 0° 6'	1.47225	0.8	39.8	91.5	1.5 vol.
2	Kumbi .	0.8911	+ 0° 5'	1.47176	1.0	47.3	90.7	1.5 „
3	Mohana.	0.8906	+ 0° 20'	1.47264	0.8	34.8	92.0	1.5 „
4	Naoli .	0.8903	+ 0° 15'	1.47205	0.5	40.7	93.0	1.5 „
5	Ragarwal	0.8946	+ 1° 20'	1.47382	0.8	38.4	88.2	1.5 „
6	Udhala .	0.8906	+ 0° 35'	1.47225	0.8	38.7	92.4	1.5 „

output of the oil without any extra cost, as it is well known even to the Indian distillers that the green fresh grass has more oil in it bulk for bulk than the late ripe grass of autumn. These improvements would go a great way to render the price of the oil more uniform.

Rectification of the oils in a rectifying steam still, whether originally obtained by water distillation or steam distillation, would give a standard uniform quality of oil, which would make the detection of adulterants very easy. If these improvements are delayed, it is possible that the Indian trade in this article may be lost.

For the purpose of this paper the following samples were taken for examination. These are described below, and the constants obtained for each are given in a tabular form on p. 276.

(1) The crude "Motia" oil obtained by steam distillation from



green grass, distilled three to five days after cutting, prepared by Mr. R. S. Pearson, Forest Economist. Distilled in October, 1914. Taken for examination from the museum of the Institute in August, 1915. The odour of the oil had gone bad, due to rancidity caused by the presence of water and other impurities. Before examination it was dried over anhydrous sodium sulphate and filtered. The constants were determined according to the methods given in "Volatile Oils," Gildmeister and Hoffman, 1st ed., pp. 185-195.

(2) No. 1 rectified by steam distillation, dried on anhydrous sodium sulphate, and filtered; 200 c.c. weighing 176 grams were redistilled, and 175 c.c. weighing 154 grams, or 87.5 per cent. were recovered as a water-white, perfectly colourless oil. Odour good, though very slightly affected by the original rancidity of the oil taken.

(3) The crude oil obtained by steam distillation from the sun-dried grass. In this case the grass was dried for about twenty-five days. It was prepared by Mr. R. S. Pearson in October, 1914. Taken for examination from the museum in August, 1915. The odour of the oil was bad owing to the presence of water. It was dried on anhydrous sodium sulphate and filtered.

(4) No. 3 rectified by redistillation with steam, dried on anhydrous sodium sulphate, and filtered; 200 c.c. weighing 177 grams gave 165 c.c. or 145 grams, or 81.90 per cent. of rectified oil. The colour was pale. Odour good, though very slightly affected by the original rancidity of the oil taken.

(5) A genuine "Motia" grass oil received from Nimar and Baldana Divisions, in the Central Provinces, distilled by water-distillation method by the Indian distillers in 1910 and stored in the laboratory. Taken for examination in August, 1915, dried on anhydrous sodium sulphate, and filtered. The odour was good. Very slight rancidity. Colour yellow.

(6) No. 5 rectified by redistillation. From 200 c.c. weighing 178 grams, only 100 c.c. weighing 88 grams, or 49.5 per cent. were recovered for analysis. Palish white; odour good.

(7) No. 5 rectified by redistillation. From 200 c.c. weighing 178 grams, 162 c.c., weighing 144 grams, or 81 per cent. were recovered for analysis. Colour pale; odour good.

Reading this table along with the table of constants as given by Messrs. Schimmel & Co., the improvement in the quality of the steam-distilled oil is evident as compared with the water-distilled oil. The water-distilled oil has a specific gravity of from

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No.	Specific Gravity at 27.7° C.	Optical rotation in 100 mm. tube (Room temperature 28° C.).	Refractive Index at 28° C.	Acid number.	Saponification number.	Ester number before acetylation.	Ester number after acetylation.	Free geraniol per cent.	Total geraniol content per cent.	Solubility in 70 per cent. alcohol. (Parts of alcohol required for 1 part of oil).
1	0.8818	+ 0° 43'	1.4705	0.41	35.9	35.49	264.1	75.6	90.5	2.40
2	0.8817	+ 0° 45'	1.4695	0.17	33.5	33.33	265.0	77.2	91.0	2.40
3	0.8831	+ 0° 26'	1.4700	0.51	35.9	35.39	264.0	75.6	90.5	2.50
4	0.8823	+ 0° 33'	1.4690	0.22	36.00	35.78	266.0	76.4	91.4	2.45
5	0.8925	+ 5° 46'	1.4765	2.11	35.3	33.9	256.6	72.9	87.6	2.58
6	0.8813	+ 0° 16'	1.4710	0.18	24.1	23.92	269.0	82.5	92.7	2.45
7	0.8918	+ 6° 57'	1.4730	0.40	34.00	33.60	260.0	74.8	88.8	2.50

0.8903 to 0.8946 at 15° C., and a five years old sample examined at Dehra Dun had a specific gravity of 0.8925 at about 28° C., while the figure for the crude steam-distilled oil is only 0.8818 and 0.8831 at 28° C. By drying the grass in sun the specific gravity of the oil distilled from it is slightly increased. It is remarkable that the old oil has given a rotation of + 5°, and the same rectified to the extent of 81 per cent. + 6°, while the rectified fraction, consisting of the first 50 per cent. of this oil, only + 0° 16'. The optical rotation in this case is high; usually the oil has an optical rotation below 1° and, very rarely, up to + 4° and even + 6°. In this case this rare maximum has been reached, the slight increase over it being due to storage and oxidation due to it. The crude steam-distilled oils rotate less than 1°, the rectified being slightly more active than the crude oils. The refractive index should be taken as fairly constant for all oils, being about 1.4700. The acid number of the crude steam-distilled oils is about double that of the oils when rectified, but it is generally less than those of the water-distilled samples.

The next important consideration is the geraniol content. The total geraniol content of the crude and the rectified steam-distilled oils is 91 per cent., the water-distilled old oil showing only 88 per cent. But *Messrs. Schimmel & Co.* have recorded a total geraniol content of 88 to 93 per cent. Parry has recorded 78 to 92 per cent. This is, of course, due to the difference in the quality of the grass distilled, which would depend on: (1) locality; (2) the climate (the total rainfall in the locality affects the quality of the oil); (3) freshness of the grass when distilled; (4) age of the grass (the over-ripe grass yields inferior oil; the "virgin" cuttings of the grass give better oil than subsequent cuttings); (5) the proportion of flowers to leaves and stem in the culms of grass taken for distillation, the finest perfume being in the flowers. But 91 per cent. total geraniol content is usual in the steam-distilled samples examined. This figure may vary slightly with locality, but it must be admitted that the steam-distilled oils will tend to be richer in geraniol than the water-distilled oils. This is further supported by the fact that in another place *Messrs. Schimmel & Co.* themselves have reported the figures given in the table on p. 278 for four pure samples of Motia oil (Parry's "Chemistry of Essential Oils and Artificial Perfumes," 2nd ed., 1908, p. 187).

In these oils 92 per cent. geraniol is the maximum, and 77 per cent. the minimum, while free geraniol varies from 68 to 83 per cent. The crude and rectified steam-distilled oils require about

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2.5 volumes of 70 per cent. alcohol instead of 1.5 volume required by water-distilled oils recorded by *Messrs. Schimmel & Co.*

## *Geraniol*

Serial No.	Combined.	Free.	Total.
1 . .	12.1	76.36	88.46
2 . .	13.55	69.98	83.33
3 . .	8.67	68.23	76.90
4 . .	8.48	83.15	91.63

The Sofia or gingergrass oil has quite different characters from those above described. They are as follows :—

Specific gravity . . . .	0.900–0.955
Optical rotation . . . .	— 30° to + 50°
Refractive index . . . .	1.4780–1.4950
Acid value . . . .	2–6
Ester value . . . .	8–55
Ester value (after acetylation). . . .	120–200

The oil is not always soluble in 3 volumes of 70 per cent. alcohol.

Palmarosa oil (*Motia*) contains as its principal constituent free geraniol, together with some geranyl esters. Methyl-heptenone and dipentene are present in traces, and possibly farnesol (*Elze, Chem. Zeit.*, 1910, 34, 857).

Gingergrass oil (*Sofia*) contains the terpenes dipentene, limonene, and phellandrene and, in addition to geraniol, perillic (dihydro-cumic) alcohol  $C_{10}H_{16}O$ . Carvone is also present, and an aldehyde,  $C_{10}H_{16}O$ , of specific gravity 0.935, not yet characterised (*Walbaum and Hüthig, Schimmel's Bericht*, April, 1904, 52; October, 1904, 41; April, 1905, 34).

Although the world's supply of these oils is produced by India, samples of oil of the *Motia* type have been distilled experimentally in Java and examined by *Schimmel & Co. (Bericht*, October, 1914; April, 1915). These oils were of exceedingly high grade, and accentuate the need for an improvement in the Indian production. Their characters were as follows :—

Specific gravity . . . .	0.891–0.892
Optical rotation . . . .	+ 0° 30' to + 0° 42'
Acid value . . . .	1.2–1.8
Ester value . . . .	37.5–51.6
Ester value (after acetylation). . . .	273–277
Total geraniol . . . .	94.3–96 per cent.

Both oils are used as perfumes, especially for soap. Palmarosa oil is also used for the separation of geraniol (*q.v.*). The oils are exported in "pots" containing up to 250 lb. of oil.

**GLOBULOL.**—This body is a crystalline sesquiterpene alcohol which has been isolated from the oil of *Eucalyptus globulus* by Smith. It is a crystalline substance melting at 88° to 89°, of characteristic eucalyptus odour.

**GLYCERINE.**—Glycerine is not a raw material of perfumery, but is used to a fairly considerable extent as an accessory to the perfume industry, so that a short description of it is not out of place. Glycerine is a trihydric alcohol of the formula  $C_3H_5(OH)_3$ , in which the hydroxyl groups can react with acids to form esters, so that three esters are possible with any monobasic acid, according to whether one, two or three hydroxyl groups have reacted. Glycerine is used to a considerable extent in certain types of face creams, etc., and should, for this purpose, be of a high standard of purity. For all practical purposes, it may be said that the world's supply of glycerine is derived from the saponification of animal or vegetable fats, which consist of the glyceryl esters of the higher fatty acids, such as oleic, stearic, and palmitic acids. The technique of fat splitting is outside the scope of this work; for detailed information in regard to it, standard works on soap making, etc., should be consulted.

Glycerine is a colourless and hygroscopic liquid, existing in a state of superfusion, since when cooled to a very low temperature, it sets to a crystalline mass, especially on continuous agitation, or by infecting it with a ready formed crystal. When so crystallised the crystals melt at about 17°. The specific gravity of pure liquid glycerine is about 1.264, decreasing by the addition of water. Commercial glycerine always contains a little water, and, in its highest degree of concentration, is sold as of specific gravity 1.260. In the analysis of glycerine the following points should be taken into account:—

(1) *Colour.*—This should, for perfumery purposes, be water white.

(2) *Odour.*—High grade glycerine should be practically odourless.

(3) *Ash.*—This should be very low, certainly not above 0.25 per cent.

(4) *Strength.*—Not more than 2 per cent. of water should be present.

The following table of specific gravities gives the strength of

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pure glycerines, that is, glycerine in which the only foreign substance present in more than traces, is water. In the case of crude glycerine, other methods of determining the strength must be used :—

Glycerine present Per cent.	Specific gravity.	Glycerine present Per cent.	Specific gravity.
100 . . .	1.2640	93 . . .	1.2455
99 . . .	1.2612	92 . . .	1.2427
98 . . .	1.2585	91 . . .	1.2400
97 . . .	1.2560	90 . . .	1.2375
96 . . .	1.2532	85 . . .	1.2242
95 . . .	1.2505	80 . . .	1.2112
94 . . .	1.2480		

Glycerine can be obtained by fermentation, but the process is not yet in a position to compete with soap makers' glycerine, but as fermentation glycerine is almost certain to be of technical importance in the near future, it may be dealt with briefly. The following details are due to K. Schweizer (*Helv. Chim. Acta*, 1919, 2, 167; and *P. & E. O. R.*, 1919, 151).

As early as 1857, Pasteur (*Comptes Rendus*, 1857, 45, 2, 1913), in the course of his classic researches, had found that during alcoholic fermentation glycerine was formed as a by-product; he obtained a yield of 3.60 to 3.64 per cent. on the sugar fermented. Later, Laborde showed that the amount of glycerine formed varied according to the quantity and species of yeast employed, and might reach as much as 7.75 grams glycerine from 100 grams sugar. The quantity of glycerine obtained depends also on the conditions under which the yeast grows; in a medium rich in nutritive matters more is obtained than in a medium less favourable to the growth of the yeast. It has further been observed that the production of glycerine does not depend on the formation of alcohol, and is in no way proportional to the latter.

F. Ehrlich considered that this trihydric alcohol might originate from certain amino-acids, as is the case with amyl and other alcohols. It has also been supposed that it is formed from the fatty substance found as small liquid drops in the yeast cells; but Buchner and Meisenheimer (*Berichte*, 1910, 43, 1782) showed that the quantity of glycerine formed was much greater than that corresponding to the free fatty acids involved, and hence concluded that the glycerine of fermented liquids must have another origin. Oppenheimer in 1914 proved that glycerine could be produced by reduction of glyceric aldehyde and of dihydroxyacetone; now these two substances are formed during alcoholic

fermentation, and indeed, according to some hypotheses, are intermediate products in the conversion of sugar into alcohol. It seemed possible, therefore, that by acting upon these compounds by a reducing agent at the moment of formation, they could be eliminated from the fermentation cycle in the form of glycerine.

The greatest difficulty was to find a species of yeast which could live in the presence of large amounts of salts, yeasts being usually very sensitive organisms. This difficulty was only overcome by using a commercial pressed yeast prepared with molasses, which gave satisfactory results. It was necessary at the same time to find a reducing agent which would not prevent the growth of the yeast.

For the study of acid reduction Schweizer made the following experiment: After having sterilised a solution of 64 grams of saccharose in 200 c.c. of water, he added 1 gram of ammonium sulphate (to supply the nitrogen necessary for the growth of the yeast), and 26 grams zinc powder as reducing agent. After making the mixture feebly acid with dilute sulphuric acid, he fermented it with 6 grams of pressed yeast. During the whole of the fermentation the mixture was kept slightly acid, and the temperature was not allowed to fall below 25°. An analysis at the end of the fermentation gave:—

Sugar . . . .	32 per cent.
Acidity . . . .	20 c.c. neutralised 0.26 c.c. normal NaOH.
Soerensen number.	10 c.c. corresponded to 3.6 c.c. N/10 NaOH.

The initial temperature was 27.5°, but after six hours it had fallen to 25°, and the yeast had not grown appreciably. With a view to assisting the growth, he added 0.5 gram of ammonium hydrogen phosphate, 0.1 gram of magnesium sulphate, and a trace of potassium sulphate. The following figures were then obtained:—

Sugar . . . .	32 per cent.
Acidity . . . .	20 c.c. neutralised 0.28 c.c. normal NaOH.
Soerensen number.	10 c.c. corresponded to 3.8 c.c. N/10 NaOH.

It was ten hours before the fermentation commenced, slowly, without becoming energetic even after twenty-four hours.

The fermentations under these and similar conditions were very incomplete, and it was necessary to abandon reduction in an acid medium.

Yeasts cannot live in an alkaline medium, and it remained, therefore, to attempt the reduction in a medium kept as neutral as possible. These conditions are fulfilled by the use of sodium sulphate in the presence of powdered chalk. For example, 64 grams of saccharose were dissolved to give a 14 per cent. solution, to which, after sterilisation, were added 0.1 gram ammonium sulphate, 0.1 gram of ammonium hydrogen phosphate, 0.1 gram of magnesium sulphate, and finally some powdered calcium carbonate. The mixture was fermented with 6 grams of yeast, the temperature being kept at about 30°. The yeast begins to develop after four hours. Meanwhile, a solution of 10 grams sodium sulphite, 0.8 gram ammonium sulphate, and 0.8 gram ammonium hydrogen phosphate in 120 c.c. of water was prepared. Every half hour 5 c.c. of this solution were added to the fermenting liquid, until all had been introduced. A very good fermentation resulted, which was complete in two days. In spite of the chalk, there was produced an acidity of 0.6 c.c. N-acid per 20 c.c. liquid.

Having thus discovered a suitable reducing agent, the influence of concentration on the course of the fermentation was studied, and for this the following solutions were used :—

(1) Sugar solutions 20 per cent. and 5 per cent.

(2) Nutritive solution: 2.5 grams ammonium sulphate, 2.5 grams ammonium hydrogen phosphate, and 0.5 gram magnesium sulphate; dissolved in water and diluted to 300 c.c.

(3) Reducing solution: 17 grams sodium sulphite in 100 c.c. water.

Each solution was sterilised by heating on the water bath during a night, and, after cooling, 5 grams of yeast were added for each experiment.

*A.—20 per cent. Sugar Solution.*

Time.	Per cent. Sugar.	Temperature.	Nutritive solution.	Reducing solution.
1st day . .	18.9	22°	30 c.c.	20 c.c.
2nd „ . .	—	—	—	—
3rd „ . .	12.8	25°	30 „	30 „
4th „ . .	5.6	26°	25 „	20 „
5th „ . .	3.9	25°	30 „	25 „
6th „ . .	4.3	26°	—	—



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Thus, in all there were added 115 c.c. nutritive solution and 95 c.c. reducing solution for an initial volume of 500 c.c., which had increased by the sixth day to 670 c.c. The growth of the yeast was not very rapid. The glycerine was determined by the method used for its estimation in wine; 100 grams sugar gave 4.5 grams glycerine.

### B.—5 per cent. Sugar Solution.

Time.	Per cent. Sugar.	Temperature.	Nutritive solution.	Reducing solution.
1st day . .	4.9	22°	30 c.c.	20 c.c.
2nd „ . .	—	—	—	—
3rd „ . .	2.3	25°	30 „	30 „
4th „ . .	3.8	26°	25 „	20 „
5th „ . .	4.2	25°	—	—

The sugar was determined, as in the previous experiment, by Balling's saccharimeter. The density of the liquid had increased, owing to the salts added and the fermentation products. The nutritive solution added was 85 c.c. in all, the reducing solution 70 c.c. The growth of the yeast was fairly good, but was much slower by the fourth day. The volume, initially 500 c.c., increased to 630 c.c. While the more concentrated sugar solution gave 0.67 gram glycerine per 100 c.c., the dilute sugar solution was found after fermentation to contain 0.32 gram glycerine per 100 c.c. The yield is thus 8.0 grams glycerine from 100 grams sugar. High concentration is therefore unfavourable to the formation of the trihydric alcohol.

But yields of this order are obtainable by simple biological processes in the absence of any special reducing agent. It was therefore necessary to make new experiments in the presence of larger quantities of sulphite. To this end 40 grams saccharose, 2 grams ammonium hydrogen phosphate, and 1 gram dipotassium phosphate were dissolved in 400 c.c. water, and the solution introduced into Hayduck's apparatus for the determination of the fermentative power of yeasts. Having added 10 grams pressed yeast, the fermentation was allowed to become appreciable, and then 30 grams sodium sulphite were added. After twenty-four hours the fermentation was finished. An intense odour of vanillin was given off by the solution. The CO<sub>2</sub> evolved was about

800 c.c., and 100 grams sugar had given 21.30 grams glycerine (mean of several experiments).

Certain biological reactions of yeast are accelerated by the presence of oxygen, and it appeared of interest to discover whether that were the case with this fermentation. As in the preceding experiment, there were introduced into a Hayduck's apparatus a solution of 50 grams saccharose in 500 c.c. water, and 10 grams pressed yeast, 30 grams sulphite being added in three portions; 1,820 c.c.  $\text{CO}_2$  were evolved, and the fermentation, without aeration, was finished in twenty-four hours. The final volume was 520 c.c., and a determination of the glycerine present gave 9.36 grams, corresponding to a yield of 18.72 grams from 100 grams sugar.

An exactly similar experiment was performed in a wash-bottle, into which was passed a current of sterilised air. After the fermentation the volume of liquid was 630 c.c., and the amount of glycerine 0.75 per cent., corresponding to a yield of only 9.44 grams glycerine from 100 grams saccharose. Without aeration, therefore, twice the amount of glycerine is obtained. This result was to be expected, since aeration favours oxidation, and thus prevents the reduction of the glyceric aldehyde and the dihydroxyacetone.

It was by this sodium sulphite method that glycerine was prepared on a commercial scale during the war by certain belligerent countries.

**GLYCERYL ACETATE.**—Glycerine  $\text{C}_3\text{H}_5(\text{OH})_3$ , being a trihydric alcohol, forms three acetic esters: glyceryl monoacetate (*monacetin*), glyceryl diacetate (*diacetin*): and glyceryl triacetate (*triacetin*). Frequently the triacetin of commerce contains some of the other two esters. This substance has no legitimate use in perfumery, but is often used as an adulterant of ester-containing oils, such as bergamot oils. For its detection, see "Esters, Artificial, Detection of."

**GOLDEN ROD OIL.**—Various species of *Solidago*, of which the best known is *Solidago odora*, yield up to 1 per cent. of an odorous essential oil containing up to 75 per cent. of methylchavicol. The oil has a specific gravity 0.937 to 0.960; optical rotation,  $+7^\circ$  to  $+14^\circ$ ; refractive index, 1.5050 to 1.5160; ester value, 6 to 10; and ester value after acetylation, 18 to 25. The oil known as Canadian golden rod oil is the product of *Solidago Canadensis*, and consists almost entirely of terpenes. The oil has little value in perfumery.

**GOUFT, OIL OF.**—The Algerian plant *Artemisia campestris*, var. *odoratissima*, yields an essential oil which is known locally as oil of gouft. It was originally examined by Jeancard and Satie (*Bull. Soc. Chim.* (3), 1904, 31, 478), and later by Roure-Bertrand Fils (*Bulletin*, 1920, 4, i., 27). It is an odorous oil containing geraniol, geranyl acetate, and pinene (probably also nopinene). The following are the characters assigned to it by the investigators mentioned :—

	Jeancard and Satie.	Roure-Bertrand.
Specific gravity . . . .	0.872 at 9.5°	0.8763 at 15°
Optical rotation . . . .	— 15° 20'	— 16° 24'
Acid number . . . . .	1.12	0.94
Ester number . . . . .	12.88	29.87
Saponification number . .	14	30.81
Saponification number (after acetylation) . . . . .	42	41.07
Total alcohols as geraniol .	11.9 per cent.	11.65 per cent.
Free alcohols as geraniol .	8.36 „	3.44 „

[Note that the table of characters on page 291 of Volume I. of the writer's work, "The Chemistry of Essential Oils, etc.," 4th edition, are assigned to this oil through the accidental misplacement of the last two lines on page 290. This table belongs, in fact, to the oil of *Artemisia herba alba*, var. *genuina*, "Scheih Oil."]

**GRAINS OF PARADISE.**—Grains of Paradise are the pungent aromatic seeds of *Amomum Melegueta*, a plant allied to ginger; the seeds have an odour recalling that of galangal. It is possible that other species of amomum are used for the collection of these seeds. The plants are natives of West Africa, where they are more or less cultivated, and are also found in the wild condition. The seeds, which were at one time known as *Melegetæ*, owe their name to the native name, corrupted from "Malaga," meaning "pepper," or possibly to the word Melle, the name of an empire in the Niger country, which may itself have the same origin from "Malaga." These seeds are also known as guinea grains or melegueta pepper. It is not an injurious drug, but in the reign of George III. an Act was passed forbidding any brewer to have it in his possession or to use it in making beer,

under a penalty of £200; and forbidding any druggist to sell it to a brewer, under a penalty of £500.

The seeds yield from 0·3 to 0·75 per cent. of essential oil, having a specific gravity about 0·894; optical rotation about  $-4^{\circ}$ ; and refractive index, 1·4912. Its ester number is about 40, and ester number after acetylation about 64. Its constituents have not been investigated.

#### GRASSES (PERFUME) OF INDIA AND CEYLON.—

There are a number of oil-yielding grasses found in India and Ceylon, and, to a smaller extent, some of them in the Malay Peninsula, Java, and other places, whose essential oils are of the highest importance to the perfumer. Some of them have not yet been exploited commercially, and may have considerable value when they are more available to the perfumer. All of these belong to the tribe *Andropogoneæ*, which is very rich in aromatic species. All of those which yield essential oils obtainable in commerce will be found described under their respective headings, such as "Citronella Oil," "Gingergrass Oil," "Lemongrass Oil," "Vetivert Oil," etc. There has, however, been a complete re-examination of the botanical relationships of these plants by Dr. Stapf (*Kew Bulletin*, No. 8 of 1906), so that the following may be accepted as the present state of our knowledge on this subject:—

According to Stapf, the aromatic character of some of these grasses is so pronounced as to have attracted the attention of man at a very early period of his history. They found a place in the performance of religious rites, among domestic medicines, in the dispensaries of the medical practitioners, and in the department of spices and perfumes. The *Schaenanthus* of the Ancients, the *Viranam* of the Vedhas, and the *Sereh* of the Malays are illustrative instances, and there is very little doubt that the much-discussed *Kalamos aromatikos* of the Greek writers was a plant of the same category, although we have not so far succeeded in fixing the species. With the discovery of more powerful or more pleasant aromas these oil-grasses gradually lost their importance or even fell out of use. But in our own day the highly perfected art of perfumery has seized on them again, has revived the taste for their odours, and created that demand for their oils which has found its response in the development of a regular oil-grass industry in Ceylon, India, and to a less degree in the Malay Peninsula and in Java. Out of the twelve grasses described here, the genus *Cymbopogon* claims ten, and *Vetiveria* and *Andropogon* contain one each.

(1) *Cymbopogon Schænanthus* was the *Andropogon Schænanthus* established by Linnæus in the first edition of his "Species Plantarum" in 1753. This plant is known as camel grass or *izkhîr* (Arabic), or *khavi* (Hindustani). As it is the *Herba Schænanthi* of the ancients and the foundation of the species, the following history, due to Stapf, is of interest :—

When in 1881 Emil Brugsch Bey discovered the tomb of Deir-el-Bahari in the necropolis of Thebes, the secret vault which contained the coffins of so many illustrious kings also yielded a remarkable profusion of botanical treasures: funeral wreaths which the kings of the Twentieth or Twenty-first Dynasty (between 1200 and 1000 B.C.) had deposited on the sarcophagi of their predecessors, offerings of fruits, lichens, bundles of a grass (*Desmostachya bipinnata*), and quantities of the straw of another grass, which Professor Schweinfurth recognised as *Gymnanthelia lanigera* (a rarely used synonym of *C. Schænanthus*). Some of the inflorescences were still in excellent condition. Even "the odour of the grass was preserved to a certain extent in the mixture of the offering." So early begins the history of the grass. Then the grass was found under similar conditions in the tombs of the cemetery of Hawara, in the Fayum, again associated with *Desmostachya bipinnata*. According to Professor Flinders Petrie, some of the tombs were probably of the Twentieth, Twenty-sixth, and Thirtieth Dynasties, but most were Ptolemaic. According to Loret, the grass is also frequently mentioned in hieroglyphic perfumery recipes as "Aethiopian cane," "rush of the Sudan," and "Cyperus of the West." Whether all of these names actually refer to *C. Schænanthus* or not, the finds of Deir-el-Bahari and Hawara afford, in any case, indisputable proof of the high place which was assigned to the grass 3000 years ago. To-day *C. Schænanthus* does not grow in the neighbourhood of old Thebes or in the Fayum; it has, in fact, with one exception, never been observed in the Nile Valley north of the Baiuda Desert (16° to 18° N.), the exception being some specimens collected by Bové in the desert near Cairo in 1829. Schweinfurth identified the *Andropogon* of Deir-el-Bahari more particularly with the article which nowadays is brought down from the Sudan and sold in the bazaars of Cairo as a medicinal drug under the Arabic name *mâhareb*.

It has been suggested that the *Kaneh bosem* or *Kaneh hattobh*, the "good" or "fragrant" reed of the Bible, was also *C. Schænanthus*. It may, of course, be assumed that the old Hebrews

knew the grass ; but how far it answered to those terms is difficult to say, considering the vagueness of the passages in which they occur. It was known to Hippocrates under the name *Schoinos*, under which name it was often used in medicine. It is quite in keeping with the general character of Greek and Roman literature that one does not meet with any serious attempt at describing the herb *schoinos*. In fact, the only reference to it which contains a descriptive element is in Dioscorides, where he gives instructions for the selection of the material : it is to be fresh, reddish, many-flowered, purplish and whitish when split apart (i.e., when the leaf bases, which are purplish and white, are pulled apart), to emit an odour like roses when rubbed in the hand, and to have a hot, pungent taste. The use of the drug continued in the West after the downfall of the Roman Empire, although apparently only for medicinal purposes, through the Middle Ages, and even into the eighteenth century, when it gradually became obsolete. We find it in the prescriptions of Aëtius (A.D. 450), and in the writings of the School of Salerno. Here the name *Palea camelorum* may have originated. At least it is attributed to Matthæus Platearius (about the middle of the twelfth century) in the various editions of the "Ortus Sanitatis," although it may, of course, be much older, as Galenus had already connected the *Schœnanthus* with the camel. In the "Ortus Sanitatis" we also find the first figure intended to represent the *Schœnanthus* or *Squinanthus*, as it is called there. It is so conventionalised as to be unrecognisable. From Brunfels (A.D. 1536) onward it is a standing article in all the herbals of the sixteenth and seventeenth centuries, and is the subject of sometimes elaborate discussions in the commentaries on Dioscorides, Plinius, and Theophrastus. It was very frequently figured in those works, the figures being drawn from the mostly barren leaf tufts as they reached Europe. Sometimes inflorescences more or less conventionalised were added. One of the earliest of those figures, by Lobel (A.D. 1576), is among the best. A very good description of the drug was given by Joh. Bauhin (A.D. 1658). Finally, in 1692, we have Plukenet's description and figure. Both are indifferent ; but they are supported by Plukenet's original specimen, which still exists in his herbarium at the British Museum, and is the typical *Schœnanthus* of the old herbalists. On this, and on this alone, Linnæus based the *Lagurus* of his "Materia Medica," which is the backbone of the *Andropogon Schœnanthus* of the "Species Plantarum." The Nabataean *Schœ-*

*nanthus* was, in the times of Dioscorides and Plinius, more valued than any other. It was called Nabataean more likely because it came *viâ* Nabatæa than on account of its growing there. In connection with this, it is interesting to note that, according to Meyer, Qûtsami's "Book of Nabataean Agriculture" actually enumerates *Idshir* (*Izkhir*, the Arabic name of *Schœnanthus*, *quâ* drug), but with the epithets "Babylonian" and "that of Hedjas," and not as Nabataean. Meyer quotes from Ibn Alawwam's "De Agricultura," who in turn quotes largely from the Arabic translation of Qûtsami's work, which was probably written in the second or third century.

Ishag Ben Amrân of Bagdad (died A.D. 903 or 905) mentions the Hedjas as the country producing the best *Izkhir*. It comes next to that of Antiochia, whilst the African is the worst. The *Izkhir* of Antiochia is evidently the "Babylonian" variety, Antiochia being merely the market whence it was distributed. Avicenna (A.D. 980-1037), too, distinguishes two kinds, the Arabian and an inferior "foreign" (*ajami*) kind. As may be expected, there is more freedom in the way in which the Arab writers treated the subject, as some of them must have known the grass in the field, or, at any rate, had first-hand evidence. Thus Abu Hanifadt (died A.D. 895) gives a description of it which could only have been made from autopsy: "*Izkhir* is a plant with a root deep down in the ground and slender, very fragrant culms, like rush or papyrus, but finer and with smaller joints. It has tufted infructescences (fruits) like the panicles of the reed, but more delicate and smaller. It is pounded and mixed with perfumes. It rarely grows solitary. Where it has settled, it may be seen to spread and cover the ground; it inhabits plains and desert land. When it dries up, it turns white." Like the old Greek doctors, the Arabs prescribed it for the preparation of unguents, theriacs—among them the famous *Electuarium Mithridatis*—and oils. Ibn Baithar quotes from the "Books of Experience" the method of preparing the latter, thus: "Take of the flowers of the grass, put them in double the quantity of oil of unripe olives . . . press the whole well and throw the flowers away; take another lot of flowers and put them in the oil. Repeat this three times in the hot season." From the Arab writers the drug passed naturally into the Persian pharmacopœias, as, for instance, the "Ulfaz Udwiye" of Mohammed Abdullah Shirazi (A.D. 1450), and the "Pharmacopœia Persica" of Frater Angelus (A.D. 1681). Whence the Persians got their supply of *Izkhir* is

not quite certain. So far the grass has been found only in a few localities in Persia, and nowhere in quantity. It was probably mostly Arabian. Still Kaempfer speaks of a "Persian and an Arabian *Schœnanthus*." Considering the part which Arabian and Persian doctors played at the courts of the Mahometan princes of India, it would be surprising if the ingredient of so many theriacs, electuaries, and other preparations had not also found its way into the Indian dispensaries. We possess a fairly full account of an instance of import of *Izkhir* under rather remarkable circumstances in Garcia de Orta and Acosta. This is what Orta, in Clusius' edition of the "*Aromata*," says: "*Juncus odoratus* grows in great abundance in the Arabian provinces of Mascat and Kalhat. The natives call it *Sachbar*, some also *Haxis cachule* (*hashish ghasul*), that is, lotion grass . . . and the flowers *Foca*. . . . With the Indians no special name has arisen; but they dub it Mascat grass, some also Mecca grass, and also camel hay. There are in those countries plenty of asses, mules, horses, etc., which know no other fodder. . . . It is imported into India for medical purposes; but the greatest quantities come with the horse dealers (of Mascat and Kalhat), who take it tied up into bundles with them in their ships to use it as litter for their horses. . . . I remember that at Diu they sold many bundles of *Juncus* for a mere trifle . . . but the natives do not appreciate it, as they are a rough and savage people, and they do not use it. We, however, and the Arab and Persian doctors employ it." The influence of the Persian physicians and the reputation of their pharmacopœias were sufficiently weighty also to transfer the foreign name, *Izkhir*, to the native drug. Not only was, and still is, the *C. Schœnanthus* of the Panjab sold in the bazaars as *Izkhir*, but the name has also passed on, with or without the qualifying epithet, *ajami* (foreign) or *Hindi*, to *Vetiveria zizanioides* (*A. muricatus*) and other indigenous aromatic grasses, so that it has become with certain writers almost a generic name. Thus the *Izkhir* of the *Abir Izkhir* of the *Ain-i-Akbari* (end of the sixteenth century) is *V. zizanioides*; the "*Taleef Sherif*" has *gundheel* (*C. Martini*) as synonymous with *Izkhir*, and the author of the "*Makhzan-el-Adwiya*" (A.D. 1771) enumerates no fewer than six Hindi synonyms for *Izkhir*, most of them vernaculars of *C. Martini*. It will be seen that the vernacular synonymy of *C. Schœnanthus* was, in India at any rate, just as confused as the scientific nomenclature of the species was up till recently.

(2) *Cymbopogon Iwarancusa*.—This grass first became known



through a publication on the *Nardus Indica*, or spikenard, in 1790 by Blane, who gives the following account of its discovery by his brother :—

“ Travelling with the Nabob Vizier on one of his hunting excursions towards the northern mountains, I was surprised one day, after crossing the River Rapti, about twenty miles from the foot of the hills, to perceive the air perfumed with an aromatic smell; and, on asking the cause, I was told it proceeded from the roots of the grass that were bruised or trodden out of the ground by the feet of the elephants and horses of the Nabob’s retinue. The country was wild and uncultivated, and this was the common grass which covered its surface, growing in large tufts close to each other, very rank, and in general from 3 to 4 feet in length. As it was the winter season, there was none of it in flower. Indeed, the greatest part of it had been burned down on the road we went, in order that it might be no impediment to the Nabob’s encampments. I collected a quantity of the roots to be dried for use, and carefully dug up some of it, which I sent to be planted in my garden at Lucknow. It here thrived exceedingly, and in the rainy season it shot up spikes about 6 feet high. . . . It is called by the natives *Terankus*, which means literally in the Hindu language ‘fever restrainer,’ from the virtues they attribute to it in that disease. . . . It is esteemed a powerful medicine in all kinds of fevers, whether continued or intermittent. The whole plant has a strong aromatic odour; but both the smell and the virtues reside principally in the husky roots, which in chewing have a bitter, warm, pungent taste, accompanied with some degree of that kind of glow in the mouth which cardamoms occasion.”

It was believed to be the spikenard of the ancients, but this is probably not true. The spelling of the name with an “i” obscures its derivation, which is from *jwara* (fever) and *ankusa* (the hook used by elephant drivers to restrain their elephants). The name thus means “fever restrainer.”

(3) *Cymbopogon Nardus*.—This grass is that producing the well-known citronella oil. Early botanists believed it to be the *Nardus Indica* of the ancients, so that Linnæus gave it the name *Andropogon Nardus*.

The citronella grass early shared the fate of the other aromatic *Andropogoneæ* by becoming almost hopelessly confused. It was Ainslie who first (1813) suggested that it was identical with the “gingergrass” of Courtallam (*C. flexuosus*) and the cultivated

"lemongrass" (*C. citratus*), and it seems to have been known for a long time by the latter name; but as "lemongrass" was very generally put down as *Andropogon Schœnanthus*, citronella was also frequently referred to by that name, chiefly by pharmacists and chemists. Then, the French name for "lemongrass being *citronelle*, the latter term also found its way into English literature, originally as a synonym of "lemongrass" in the wider sense, and later on more especially of the "Ceylon lemongrass," that is, *C. Nardus*. Pereira (1850) seems to have been the first to use the term "citronelle oil" as equivalent to "lemongrass oil."

J. Bell, in his notes on the London International Exhibition of 1851, mentions "oil of cintronelle, or oil of lemongrass." He stated that it was imported from India, "and is the produce of a grass known to botanists as *Andropogon citratus*, and by some persons considered to be identical with *Andropogon Schœnanthus*." In the Ceylon Catalogue of the Parish Exhibition of 1855, p. 17, we find two distinct oils: (1) lemongrass oil, from *A. Schœnanthus*, and (2) "citronella oil; citron oil; perfumery," and against the latter there is in the Kew copy an entry in Alex. Smith's handwriting: "Citronella oil, *Andropogon*." W. S. Piesse, in his "Art of Perfumery," 1855, p. 31, also refers to "citronella," saying: "Under this name there is an oil in the market, chiefly derived from Ceylon and the East Indies; its true origin we are unable to decide. In odour it somewhat resembles citron fruit, but is very inferior. Probably it is procured from one of the grasses of the *Andropogon* genus." Gladstone (1872) and C. R. A. Wright (1874) were the first to examine, under the name of "citronella," the oil of *C. Nardus*, as is evident from their descriptions of the oil, but both referred it to *Andropogon Schœnanthus*. Even as late as 1880, it was confused with *C. flexuosus* and *C. citratus* by Bentley and Trimen, who figured a specimen of the former as *Andropogon Nardus*. In 1883 "citronella" was at last clearly confined to *Andropogon Nardus* by Watt, who gives the average exportation of citronella from Colombo as amounting to about 40,000 lb.; the exact return for 1864 was 622,000 oz.

Outside Ceylon *A. Nardus* has been in cultivation for some time in Penang, whence citronella oil is mentioned as early as 1872 by Gladstone, and in the Straits Settlements and Java. When it was introduced into the Malay Peninsula and Java is uncertain, but it cannot have been very long ago. McNair, in his book, "Perak and the Malays," 1878, p. 73, speaks of "the

flourishing growth of citronelle and lemongrass, from which essential oils are extracted," as worth mentioning; but in 1886 Cantley complains of the insufficient attention which the cultivation of these two grasses receives in the Straits, and in 1900 the total area of citronella estates in the peninsula was estimated at only 2,000 acres at the highest. In Java it is mentioned by Romburgh in 1892 as *Roempoet sereh wangi* under *A. Iwarancusa*, and is stated to have been introduced into the "Cultuurtuin" in 1891. He drew the attention of Schimmel & Co. to the oil prepared from the Javanese crop; this reference eventually led to the establishment of citronella distilleries in Java. According to Gildemeister and Hoffmann, both the Malay Peninsula and the Java grass represent the *Maha Pengiri* variety (see below). Quite recently experiments in growing citronella grass have been made in the West Indies.

Two kinds of citronella grass have recently been distinguished by the growers: *Maha Pengiri* (the Great Pengiri), and *Lenabatu* or *Lana Batu Pengiri*, or, briefly, *Lenabatu*. The former is also known as "old citronella grass," or "Winter's grass," because it is now almost exclusively grown by Messrs. Winter & Son; the other is spoken of as "new citronella grass." Specimens of both varieties received at Kew from Galle, so far as they go, do not show any morphological differences. The old citronella grass is described as a surface feeder, which soon grows out of the ground and gets exhausted, dying off after ten or fifteen years of cultivation; and it has somewhat broad leaves, and the bushes formed are larger than the second (i.e., *Lenabatu*). It yields a finer oil, but the necessity of frequent replanting has led to its being more and more replaced by the *Lenabatu* variety.

*C. Nardus* in its typical form is only known in the cultivated state. It is an awnless grass; the valve or flowering glume of the hermaphrodite spikelet being either entire or more or less bifid, with a minute point or a very fine and short bristle from the sinus. The flowers are usually apparently normal, but do not seem to set freely, and in some cases all the spikelets are male or otherwise imperfectly developed, or they are infested with *Ustilago*. On the whole, the reproductive system seems to be debilitated. This is the case with all the specimens I have seen, irrespective of their origin, and is evidently the result of the treatment the grass has experienced from the grower, in whose interest it is that they should not flower, as, according to Gildemeister and Hoffmann, "otherwise the tufts become too dense, become yellow within,

and spoil." Still, a certain amount is allowed to seed for renewing the plantations, the usual mode of propagation being apparently by dividing the bushes. The reduction or suppression of the awn is no doubt in correlation with the partial sterility of the cultivated *C. Nardus*, the wild ancestor of which we have to seek among the awned forms. It has very generally been assumed that the citronella grass is a descendant of the wild *Mānā* grass of the Ceylon Patanas, but it is unfortunate that there is no specimen at Kew which is definitely stated to have been collected in the wild state. Sir Joseph Hooker, however, who had the grasses of the Peradeniya herbarium at his disposal when working out the *Gramineæ* for Trimen's "Handbook of the Flora of Ceylon," says that there were three specimens of the wild *Mānā* in that collection from Galle, Maoya, and Peradeniya, and they were all Hackel's *Andropogon Nardus*, var. *nilagiricus*. Willis also states that the *Mānā* of the *patanas* is distinct from the cultivated citronella grass, but does not say how it differs. Now there is at Kew a suite of excellent specimens of the cultivated awnless *C. Nardus* from Mr. Jowitt's estate at Bundarawalla, and, sent with them at the same time and from the same locality, and numbered concurrently with the first, is another set which is undoubtedly *Andropogon Nardus*, var. *nilagiricus*. Whether they grew wild on the estate or were in cultivation is not stated. A careful comparison of both sets has convinced me that this *Andropogon Nardus*, var. *nilagiricus*, is, as Sir Joseph Hooker has stated, actually the mother plant of the *Pengiri Mānā*, or citronella grass. Gildemeister and Hoffmann state, on Mr. Winter's authority, that the *Maha Pengiri* came from Malacca. As the citronella grass is a comparatively recent introduction to the Malay Peninsula, and certainly does not occur there in the wild state, this can only mean that it has, possibly as an improved race, been reintroduced into Ceylon from Malacca; but, as the *Maha Pengiri* is at the same time put down as the old or original citronella grass of Ceylon, it is more probable that the statement is due to some mistake. As to the *Lenabatu* variety we have more precise information. It originated about 1885 near Matura, in south Ceylon, presumably in a plantation, and in a short time almost entirely replaced the old grass, on account of its being so much hardier. Mells says of it: "It is in general appearance very like the *Mānā* grass found on *patanas* up country."

(4) *Cymbopogon confertiflorus*.—This grass is in all probability the parent plant of the citronella grasses. In Ceylon it is one of

the most conspicuous elements of the vegetation of the *patanas*; In strong sunshine it emits an overpowering odour of citronella. The Cingalese name for it is *Mānā*, whilst it is called *Bamte* in the Nilgiri vernacular.

(5) *Cymbopogon flexuosus*.—This grass, formerly known as *Andropogon flexuosus*, Nees ex Steud., is known as Malabar or Cochin grass, and is distributed in the Tinnivelli District and in Travancore, and during the past few years a large acreage has been planted with the grass.

According to Stapf, Rheede, in his "Hortus Malabaricus," described a grass under the name *Kodi-pullu*, and its illustration is that of a grass very common throughout Travancore and the adjoining district of Tinnivelli. Rottler knew it, and put it down, though with some doubt, as *Andropogon Nardus*, which it resembles very much indeed. Ainslie (1813) mentions it as *Sukkanaropilloo* and "gingergrass" (the exact equivalent of the Tamil name), and says of it: "This is a variety of the grass which is well known in Lower India by the name of the lemongrass; it differs, however, from it in this respect, that, on being chewed, it has a strong flavour of ginger. It is very common on the Courtallam Hills in the Tinnivelli District, where the natives consider an infusion of it as stomachic and febrifuge." And later on (1826) he adds: "The natives occasionally prepare with it an essential oil." This, I believe, is the first record of oil being prepared from Malabar grass. Klein collected the grass in 1818 on the same hills, and his specimens, which are also marked "*Suckunari pillu*, Tam.; gingergrass, Ang.; *Andropogon Nardus* (?)," leave no doubt as to its identity with the plant from which the Travancore or Cochin lemongrass oil is produced. Wight subsequently distributed specimens of the same grass as "*Andropogon flexuosus*, N.E." It was not, however, described until 1855, when Steudel published a description, retaining for it Nees' name; but not much notice was taken of Steudel's species, which, if mentioned at all, was usually cited as a synonym of *Andropogon Nardus*, as, for instance, by Bentley and Trimen, who, moreover, figured it as *Andropogon Nardus*. In 1889, Hackel distinguished it as a variety of the typical *Andropogon Nardus* (citronella grass), and the same place was given to it by Hooker in the "Flora of British India," but neither author connected it with the lemongrass oil of Travancore, which very generally was treated simply as "lemongrass oil."

Morphologically, *C. flexuosus* differs from the other species of

the *Nardus* series by its large, loose, greyish or slate-coloured panicles, the branches of which are particularly slender, long, flexuous, and often drooping, and by the less conspicuous spathes and the smaller, usually very slender and acute, spikelets. The basal leaf sheaths are rather narrower than those of *C. Nardus* and *C. confertiflorus*, and are not reddish within.

When the Malabar grass oil—this name, which is used in Barber's collection, is preferable to the name Travancore lemon-grass oil—was first exported cannot be decided precisely ; but the "lemongrass oil" mentioned by Pereira (1850) as imported into England from Cochin was very likely the oil of *C. flexuosus*, and not of *C. citratus*. In 1859, Major Heber Drury, writing to D. Hanbury and referring to a specimen of *C. flexuosus* which he had sent him, says: "From this species (and from this only) lemongrass oil is distilled in Travancore." Four years later Hanbury received the same plant from E. G. Waring, with this note: "*Andropogon* (?), which yields the lemongrass of Travancore—abundant on the plains—is not cultivated." The statement in the "Pharmacographia Indica," vol. iii., 1893, p. 565, that the oil is distilled in Travancore from Anjengo northwards, and that the grass is burnt at the end of the dry weather, no doubt also refers to *C. flexuosus*, and not to *C. citratus*, as the authors of that work believe. It is probably due to this confusion that Gildemeister and Hoffmann say, quoting Dymock, Warden, and Hooper as their authorities, that "the grass is *cultivated* on a large scale only on the Malabar coast in Travancore, on the western slope of the mountains, north of Anjengo." Mr. T. F. Bourdillon writes quite recently from Quilon that only within the last year or two extensive areas have been planted up with the Malabar grass. As the Travancore grass oil is not commercially distinguished from the oil of *C. citratus*, both being sold as lemongrass oil, it is difficult to decide as to which oil published analyses refer. At all events, according to Stapf, the soluble East Indian lemongrass oil is derived from this grass.

(6) *Cymbopogon coloratus*.—This grass has a powerful lemon-grass odour, and is found from the Tinnivelli District to the Anamallai Mountains, and also in the Madras Presidency. It may be sometimes mixed with *C. flexuosus* for distillation purposes.

Practically nothing is known of the conditions under which this grass grows ; but it has a distinctly xerophytic habit. It is a highly aromatic grass. There is, however, no evidence that it is

used for extracting oil or for any other purposes, unless it is one of the "lemongrasses" of the Malabar district to which the following extract from the *Madras Mail* refers : "The natives of Ernad and Waluvanad empirically distinguish no fewer than twenty-seven species of lemongrass, but say that only five of these varieties possess a commercial value. They also state that the most valuable of these varieties does not blossom. Ernad and Waluvanad, I am reliably informed, are full of hills, on which lemongrass grows wild and could be had virtually for the collecting." The variety which does not blossom is very probably *C. citratus*.

(7) *Cymbopogon citratus*.—Stapf is of opinion that this plant is that from which the lesser soluble lemongrass oils are distilled. Formerly known as *Andropogon citratus*, it is referred to by Samuel Browne in his "Seventh Book of East Indian Plants" in the following terms :—

"This is a most delicate sort of *fragrant Grass* which being rubbed smells like *Baume* and *Lime* or *Limon peel* together. The *Portuguese Women* fume their children with it, and give the *Decoction* of it with other things for *Fevers* and to strengthen weak stomachs ; but the Natives use it not, which together with its growing in *Gardens* on the Sea coast and not up the Country, as I can yet observe, makes me think the Portuguese brought this from other parts and planted it here ; certainly, so excellent a Plant of such *Fragrant* and *Aromatic taste* must have many *Vertues*. I use it in many cases, and generally with success. While I was writing this, in came a Person, who says, that about 30 years ago, viz., about 1666, one Antonio Palia, brought 3 Pots of this Grass from Batavia to Paliacut, one of which he sent to a Garden, here at Madrass."

The Portuguese in India termed it *Herba cheirosa*, the equivalent of the Tamil *Vasana-pillu*, and the Dutch named it *Serek*, a name by which the grass is still known in Java.

It is probable that the grass was introduced into Ceylon during the Dutch occupation of the island.

The comparatively recent date of the cultivation of the lemongrass in India is evident from the nature of the established vernaculars. The Tamil *Vasana-pillu* is merely the equivalent of the Portuguese *Herba cheirosa*, under which name it was probably introduced. The term was taken up unchanged, or almost so, in Malayalam, Canarese, and Telegu. Another Tamil name, *Karpūra-pullu* (camphor grass), is equally descriptive, and

the same applies to the Gujerati and Marathi vernaculars, which mean "green tea," whilst the Dukni name given by Ainslie, namely, *Naring ke bās ka ghans*, is a direct translation of "lemon-grass."

The plant was sufficiently attractive in India to cause its early introduction into the colonies of those European powers which had possessions in India. It was introduced into Jamaica at the end of the eighteenth century, and later into the Spanish and French colonies, and, probably through the Portuguese, into East Africa. In the Malay districts it is universally grown as a medicinal and kitchen herb. Its history there goes back, no doubt, far beyond the arrival of the first European invaders. We hear of it almost simultaneously from the Philippines and from Java as early as the first half of the seventeenth century. In 1635, Juan Eusebius Nieremberg, a Spanish Jesuit in the Philippines, describes it quite unmistakably under the name of *Tanglat* a term still in use for "lemongrass" in the Tagalog and Visayan dialects (spelt *Tañglad*). The passage, which is worth quoting, reads: "*Tanglat*. It is a herb springing from a bulbous root, the swollen base of the leaf tufts, whitish-red without, yellowish within; from it rise 10-12 leaves, about 1 m. long, rather rough and moderately green; there is, however, neither a (flowering) stem nor fruit. The whole plant has a scent like that of lemon flowers, but stronger. Cooked, it improves the taste of stale boiled fish; put into wine it gives a pleasant flavour, and it imparts a delicious odour to sauces and spices. The liquor distilled from it is almost scentless until exposed to the sun; but this being done, it usually exhales a pleasant odour, and applied to the face seems to sharpen and invigorate all senses and the head."

Stapf summarises the uncertainty of the origin of the grass as follows:—

"As the lemongrass is only known in the cultivated state, the question arises, what is its origin? I am afraid it is yet too soon to give a satisfactory answer. It is true there is not, among the Malayan species of *Cymbopogon*, so far as I know them from the collections at Kew and the British Museum, a single one which suggests itself to my mind as the spontaneous state of the lemongrass, and Rumphius' statement that it occurs in the wild state in Amboina is open to doubt; but our knowledge of the *Cymbopogons* of the Malayan region is still so imperfect that the possibility of the lemongrass having originated there is by no means excluded.

"The *Cymbopogon* most closely approaching *C. citratus* that I



have seen is *Cymbopogon pendulus*, Stapf (*Andropogon pendulus*, Nees ex Steud.), collected by Wallich in Nepal, by Hooker, Kurz, and Clarke in the Sikkim Terai, and by Griffith (No. 6763) in 'Bengala.' No vernacular name is given, there is no information concerning its properties and uses, nor has it ever been connected with the lemongrass, and to do this, in the light of our present knowledge of the history of the latter, would involve a hypothesis bolder than I dare to advance. Another allied form, presumably from the same region, but less like lemongrass, and distinguished therefrom by less hairy racemes, borne on long common peduncles, which are frequently exserted from the supporting sheath, and by smaller as relatively much broader spikelets, was figured as '*Andropogon Schoenanthus*' (qua 'lemongrass') by Wallich, and referred to *Andropogon Nardus*, var. *exsertus*, by Hooker. It was in cultivation in the Calcutta Botanic Garden, and may have been raised from the seeds of a fairly distinct *Andropogon* of the *Nardus* series, which extends from the Saharanpur Terai to the Garo Hills, and possesses very aromatic citron-scented leaves. However this may be, neither Wallich's plant nor its presumably wild representative agrees sufficiently with the lemongrass to suggest the derivation of the latter from either of these species."

(8) *Cymbopogon Martini*.—This grass is the plant from which palmarosa and gingergrass oils are obtained. The differences between the two oils are so pronounced that some marked difference between the distillation materials must exist. It has been suggested that the period of growth at which the grass is cut is responsible for the difference in the oils. But this is highly improbable, and it seems certain that there are two varieties of the grass, whose morphological differences are not yet settled. The following account of the foundation of the species is given by Stapf, the grass having been originally named *Andropogon Martini*. It is known in India to-day as *Rusá* or *Rosha* grass:—

During the war of 1790–1792 against Tipu Sultan, Claude Martin, who joined the expedition in 1791 as a Commissioner of provisions and aide-de-camp to Lord Cornwallis, collected "in the highlands of Ballaghat" the seeds of a grass which had struck him, owing to its excellence, as a fodder plant, as well as on account of its pungent taste and aromatic odour, which was so strong as to impart itself to the milk of the cows which fed on it. From the seeds he raised an abundant crop at Lucknow. He also supplied Roxburgh "with a small stalk, roots and seed." The "small stalk" is not preserved; but Roxburgh grew the grass

from the seed in the Calcutta Botanic Garden, and of the specimens thus raised there are two at the British Museum, one from Roxburgh's herbarium, the other from General Hardwicke's collection. The first is named "*Andropogon Martini*" in Roxburgh's own hand; the other, under the same name, bears the date February 18th, 1789. The name did not appear in print until 1814, whilst the description, although evidently written before 1799, was only published in 1820.

Dr. Maxwell, Assistant Surgeon at Asirgarh Fort, in Nimar, wrote, in 1824, a letter to the Medical Board of the East India Company, in which he called attention to a fragrant grass which was "found in great abundance on the sides of the hill fort, as well as all over Malwah. From it," he says, "is extracted a highly pungent essential oil (when in its pure state), which I can from experience confidently recommend as of the highest benefit, when applied by friction, in rheumatic affections," and, further, that "it is prepared by a very rude process under Jaum Ghaut, in the vicinity of the station of Mundlaisir." The specimens which he sent with his letter were submitted to Wallich, who, in his reply to the Medical Board, reported as stated above, adding that he himself had found the plant abundant in Nepal. In the following year, J. Forsyth, who had been directed to investigate the matter on the spot, presented a paper to the Medical and Physical Society of Calcutta, in which he gives a detailed account of the preparation and the sale of the oil and the conditions under which the grass grew and was gathered. He also gives *Roosa-la-Tel* as the native name of the oil. Of the grass, he reports that it "is met with in frequent distinct patches in the jungle throughout the province of Nemaour, but in greatest abundance along the foot of the Vindhya Range, near Nalcha, at which two places only, I believe, it is prepared, at least to any amount. About the latter end of August it begins to bud, and continues to flower in tolerable vigour till the end of October, during which period alone it gives out the oil in sufficient quantity to cover the expense and trouble of its preparation, as after this it speedily dries up, and what little oil it does yield is extremely acrid, and unfit for use. . . . The oil is obtained from the grass by distillation . . . the plant is cut across where it begins to give out its flower, and bound up into small bundles. . . ." A few years later (in 1830), Charles Hatchett, F.R.S., a prominent chemist, received a sample of oil from a Mr. Samuel Swinton, who had been in the East India Company's service for many years and had resided for some time

in Malwa. Hatchett made the grass which yielded this oil the subject of a somewhat confused paper, entitled "Spikenard of the Ancients" (1836). Swinton, like Maxwell, first became acquainted with the oil (which he says is called *Rhonsee-ke-Tell* by the natives) as an effective remedy in severe attacks of rheumatism. He also stated "that although the plants are found in other parts of India as well as in Malvah, yet those which grow about the Jaum Ghaut are preferred, and gathered in the month of October, when the seeds forming the ears or spikes have become fully ripe. At that season, however, in the places where this gigantic grass is produced, the jungle fever is so prevalent that the peasantry who collect it will not expose their health . . . unless tempted by very high remuneration. . . ." Hatchett further adds: "Mr. Swinton was informed by them (the principal natives) that it has been prepared in and about Malvah from time immemorial, at first probably by the Parsees, although at present it is entirely in the hands of the Borahs, a very commercial people, forming a sect of Moslems, whose chief resides at Surat. The oil is obtained from the spikes, which, when ripe, are cut with a portion of the stem about 1 foot in length, and are then subjected to distillation. Only a small comparative quantity of the oil is consumed by the natives, the greater part being now, as was the case in very remote times (according to tradition), sent as an article of commerce to Arabia." Finally, it is stated that "the odour of the plant is so powerful that, although camels will eat almost any vegetable, yet they will not browse on this. . . ." Neither the production nor the export of the oil can, however, have reached any considerable dimensions, as Jacquemont, who, in the spring of 1832, visited Nalcha and Jaum, and gave a very full account of Malwa, does not mention the grass or the oil. The grass, it is true, might have escaped him, as at that season it must have all been dried up.

How far there is any truth in the tradition that oil has been distilled from the *Rusá* grass "from time immemorial" we do not know. The authors of the "Pharmacographia Indica" (vol. iii., p. 558) merely suggest that "the industry commenced in the eighteenth century, whilst Khandeish was in a flourishing condition unders its Mahometan rulers." However this may be, there is sufficient evidence that the grass must have been known to the Aryan peoples of India for a very long time. *Rohisha*, the Sanskrit equivalent of the Hindi *Rusá*, occurs in "Suśruta" and in some of the earliest Sanskrit dictionaries. Another name

in Sanskrit, evidently from the same root, is *Rósem*. Variants of these terms are generally recognised vernacular names in the Hindi, Gujarati, and Mahrati dialects. Curiously enough, the name does not appear in the earlier Persian pharmacopœias, the first record of it, *Rús*, being apparently in the "Makhzan-el-Adwiyah" (1771). According to the authors of the "Pharmacographia" (vol. iii., p. 557), *C. Martini* is also "the *Bhustrina* or *Bhutrina* ('earth grass') of the Raja Nighanta," and among the synonyms which it bears we may mention *Gandha-Khêda* and *Gandha-trina* ("odorous grass"), *Su-rasa* ("well-flavoured"), and *Su-gandha* ("having an agreeable odour").

(9) *Cymbopogon cæsius*.—This grass, formerly known as *Andropogon cæsius*, or *Kamakshi* grass in Tamil, very closely resembles the *Rusá* grass or geranium grass used for distilling palmarosa oil. In the Carnatic the *Rusá* grass is replaced by a closely allied form with more slender and more branched culms, usually from  $\frac{2}{3}$  to 1 metre high, with narrower, thinner, often almost flaccid and very glaucous leaves, and with generally smaller panicles, which seem to retain their glaucous colour, or merely turn straw colour when mature. The structure of the spikelets is, however, that of *C. Martini*, and so closely does the Carnatic grass in some instances approach the narrow-leaved state of *C. Martini* that there would be no difficulty in constructing a chain of intermediate stages, linking together both forms as completely as possible. Those transition forms are, however, so far as I can see, confined to the border districts where the two grasses meet; elsewhere they are sufficiently distinct.

The oldest specimens of the Carnatic grass on record are a specimen in the Plukenet herbarium at the British Museum, and several in the Du Bois herbarium at Oxford, all of them collected near Madras at the end of the seventeenth or in the early years of the eighteenth century; but it is very probable that a passage in a letter by Herbert de Jager to Rumphius, dated July 6th, 1683, also refers to it. Contesting the view of Bontius and others that the *Serek* of the Malays is identical with the *Schœnanthum* of the herbalists, and, in support of his argument, he says: "I have become familiar with the true and genuine *Schœnanthum* in Persia, and particularly on the coast of Coromandel, where I have traversed whole fields of that grass, which is about  $2\frac{1}{2}$  to 3 feet high, and the scent of which may be noticed from afar, particularly during the night, when dew falls, or in day-time when it rains, whilst in sunshine and fine weather not much

odour is perceptible. In Golconda this *Schœnanthum* ground into powder is used for washing the hands on account of the sweet scent it imparts to the water ; though the odour does not persist when the hands get dry." Neglecting for the present the question as to what the *Schœnanthum* powder of Golconda was, there can be little doubt that the fragrant Coromandel grass, of which there were whole fields to traverse, was the *Kāmātcī-pillu* of the Tamils. Of this name we hear for the first time in Samuel Browne's "Seventh Book of East Indian Plants," edited and commented on by Petiver (1702). The plants which form the subject of the paper were collected "between the 15th and 20th June, A.D. 1696, in the ways between Fort St. George and Trippetee, which is about 70 miles off." One of them was *Comachee pillee*, and of it Browne says : "This is Schoenanth, which the natives here have not in great Esteem ; sometimes in the Moors' Camps, the Horses, Camels, and Oxen which carry burthens eat nothing else ; it is generally 2 or 3 feet high here about (but near Color in reech soyl, I have seen it 8 feet high) [this gigantic grass is no doubt *C. Martini*] and thick as a Quill or small Reed ; It's sometimes by the natives put into their Decoctions for Fevers, and with us is deservedly of more esteem." Petiver identified the *Comachee pillee* with Plukenet's *Gramen Dactylon Maderaspense*, figured on Plate 119, Fig. 2 of his "Almagesta" (1691), the type of which is in Plukenet's herbarium—it is the specimen referred to above.

*C. cæsius* seems to inhabit the greater part of the Carnatic, from the extreme south to the Chingalpat District. It is evidently common, on the whole, in that region, but little use seems to have been made of it so far, except as an occasional domestic remedy. There is, however, among the specimens communicated by Mr. Barber, one with a note to the effect that it is the "grass from which Mr. Proudlock has been distilling oil." A short account referring to it is contained in the "Administration Report of the Government Botanic Gardens and Parks, the Nilgiris," for 1901, p. 5. According to this report, the grass was obtained from Arni, in the North Arcot District, where it is stated to grow in great abundance. The yield of oil from a freshly cut sample received at the end of December was 0·431 per cent. Another and larger quantity, which was received in April in a thoroughly dry condition, yielded 0·711 per cent. of oil, the differences in the yield being attributed to the first lot being fresh, whilst the other was dry.

(10) *Cymbopogon polyneuros*.—Just as *C. Martini* is replaced in the south-east of the Deccan Peninsula by *C. cæsius*, so another species takes its place in the south-west. This species, *C. polyneuros*, is, however, much better defined than *C. cæsius*. It is a moderately robust grass with a tendency to copious branching from the collar so as to form dense tufts of culms, with somewhat persistent narrow basal sheaths, rather fat, smooth blades with a rounded base, more or less glaucous beneath, and often suffused with purple along the margin, and with short, contracted variegated panicles, the herbaceous sheaths being usually deep brown-green with a narrow scarious margin, the spikelets being green in the lower part, and more or less blackish-purple in the upper. It was first distributed by Wight (No. 1705) under the name *Andropogon versicolor*, N.E., a name chosen, no doubt, in allusion to the variegation of the inflorescence. Nees never published a description of it. On the other hand, Steudel has, in his "Synopsis Plantarum Graminearum" (1855), p. 388, an "*Andropogon versicolor*, Nees MSS.," under which he quotes "*A. Schœnanthus*, Wall. Cat. n. 8794L." Wallich's "Cat. n. 8794L." is in Wallich's own herbarium identical with n. 8794K., which Steudel (*loc. cit.*) cites under *Andropogon clandestinus*, Nees. Steudel's description of *Andropogon versicolor* agrees neither with Wight's No. 1705, issued as "*Andropogon versicolor*, N.E.," nor with Wallich's n. 8794L. It is not clear what the plant which Steudel had in mind was; it cannot well have been Wight's "*Andropogon versicolor*, N.E." Wight does not indicate the locality where his No. 1705 was collected beyond the general note "Peninsula Ind. Orientalis." It agrees absolutely, however, with a grass which has frequently been collected in the Nilgiris, among others by Hohenacker, who distributed it as "933, *Andropogon* (*Cymbopogon*) *nardoides*  $\beta$  *minor* N. ab E.,"; this was made by Steudel the type of his *Andropogon polyneuros*. That name being perfectly unambiguous, its specific component will have to be retained for the Nilgiri grass in question in preference to *versicolor*, although the latter has very generally been applied to it. Outside the Nilgiris, *C. polyneuros* has so far only been observed in Ceylon, where it is, particularly at higher elevations (up to 1,500 metres), a locally common plant. Thwaites has already called attention to the "rather agreeable aromatic odour" of the inflorescences of this species, adding "that the essential oil appears to be situated principally at the base of the spikelets." According to a note in the *Tropical Agriculturist* for 1901

(p. 873), the odour of the crushed leaves resembles that of fennel or anise.

(11) *Vetiveria zizanioides* is the *cus-cus* or *khas-khas* grass, from which vetivert oil is produced. It was formerly known as *Andropogon muricatus*. In the wild state it is distributed over most of British India and Ceylon, being found on the banks of rivers and on rich marshy soil up to an elevation of 1,800 feet. It is sometimes cultivated, as, for example, in Rajputana and Chutia-Nagpur. It is cultivated in the Malay districts, the West Indies, Brazil, and Réunion.

The Hindu name for the grass is *khas-khas*, the name "vetivert" being of Tamil origin. Jones in 1795 identified the *Usira* of Kalidasa with *khas-khas*, and Hessler did the same in his translation of the "Ayurvedas."

The natural area of this grass in India and Ceylon includes practically the whole country in the north up to altitudes of 600 metres. Although common in many parts of the country, particularly on the banks of rivers and in rich marshy soil, it is also at present, as in Rheede's time, occasionally cultivated, as, for instance, in Rajputana and in Chutia-Nagpur. Eastwards the area extends into Burma. Throughout the Malayan region, however, it occurs only in the cultivated state or as an escape from gardens. It has also been introduced into the Mascarenes, the West Indies, and Brazil; but it seems that in these countries oil is not distilled to any appreciable extent, except perhaps in Réunion, where the grass must have been in cultivation for at least 100 years, as the first sample of vetivert oil that was chemically examined (in 1809) came from there. (See also under "Vetivert Oil.")

(12) *Andropogon odoratus*.—This grass, known in India as *Usadhana*, is a little-known grass which was discovered by Dymock at Thana in 1875, and mentioned on account of its strong odour of ginger under its vernacular name, *Usadhana*, in the first edition of his "Materia Medica of Western India" (p. 693). In the second edition of that work (p. 853) it was referred to *Andropogon Nardus*. Subsequently it was, however, recognised as a new species by Mrs. J. C. Lisboa, and described as *A. odoratus*. This very aromatic grass is used by the peasantry of the Thana District for medicinal purposes. An essential oil of a golden-yellow to a deep sherry colour, with a distinctive odour, was obtained from it by distillation, but it has not yet become an article of commerce. The odour is, according to the "Pharmacographia

Indica," vol. iii., p. 570, at first that of cassia and rosemary, but afterwards that of oil of cassia or, according to Gildemeister and Hoffmann, that of pine-needle oil.

**GRIFFES DE GIROFLE.**—The flower stalks of the cloves, separated whilst they are drying, are known in Zanzibar as *Vikunia*, and in France as *Griffes de Girofle*.

**GUAIAECUM WOOD OIL.**—See "Bulnesia Sarmienti, Oil of," and "Champacol."

**GUAIAOL.**—Although this body has not any odour value, it is of interest as being the only well-identified constituent of the so-called guaiacum wood oil—the oil of *Bulnesia sarmienti*. It is a sesquiterpene alcohol, of the formula  $C_{15}H_{26}O$ , melting at  $91^{\circ}$ , of specific gravity 0.9714 at  $\frac{20^{\circ}}{4^{\circ}}$ , and having a refractive index 1.5100 at  $20^{\circ}$ , and specific rotation about  $-27^{\circ}$ . (See also Gandurin, *Berichte*, 41, 4359).

**GUM THUS.**—See "Boswellia Resin."

**GURJUN BALSAM OIL.**—Gurjun balsam is an oleoresin derived from various species of *Dipterocarpus*. It is a viscous substance closely resembling balsam of copaiba in general characters, and is used to some extent as an adulterant of copaiba. It has no direct relationship with legitimate perfumery, but is found as an adulterant of many essential oils. The oleoresin, on distillation, yields about 50 to 60 per cent. of an essential oil, having a specific gravity 0.915 to 0.935; optical rotation,  $-30^{\circ}$  to  $-135^{\circ}$ ; refractive index, about 1.5050; acid value, 0 to 1; and ester value, 4 to 8.

Gurjun oil is a colourless liquid of sharp odour, but of no value as a perfume material. It is, however, of interest on account of the fact that it has been used to a considerable extent as an adulterant of Indian palmarosa oil. It is easily detected by analysis in this oil; and as palmarosa oil is used as a raw material for the production of geraniol, traces of the adulterating gurjun oil remain in the geraniol produced from the palmarosa oil. Geraniol so produced is used to some extent as an adulterant of otto of rose, and if the adulterating geraniol has, in fact, been manufactured from palmarosa oil already adulterated with gurjun balsam oil, traces of the adulterant are easy to detect in the otto of rose. Gurjun oil, or any oil containing more than traces of it, gives the following characteristic colour reaction, which is a practically definite proof of the presence of the oil as an adul-



terant. If 5 to 10 drops of the suspected oil are added to a mixture of 10 c.c. of glacial acetic acid containing about 5 drops of nitric acid, a violet colouration will result almost immediately. If no colour results within one minute, it may be taken for granted that this adulterant is absent. This oil has no interest to perfumers other than as an adulterant, as above indicated.

**HARDWICKIA BALSAM.**—The so-called African copaiba is of no interest to the perfumer, except that the essential oil distilled from it is from time to time used as an adulterant of perfumery oils. There is considerable doubt as to the botanical origin of the balsam. It is usually ascribed to *Hardwickia Mannii*. It has also been said to be the product of *Oxystigma Mannii*, and it has recently been suggested that it is derived from *Daniella thurifera*. It is a thick, viscid oleoresin, containing about 40 to 55 per cent. of essential oil. The characters of the balsam are as follows: specific gravity, 0.985 to 0.998; acid value, 55 to 65; ester value, 6 to 10. It is also known as illurin balsam. The essential oil is a colourless liquid having the following characters:—

Specific gravity	. . .	0.915–0.932
Optical rotation	. . .	+ 5° to + 37°
Refractive index	. . .	1.5000–1.5060
Acid value	. . .	5–10
Ester value	. . .	0–6
Ester value after acetylation	. . .	Up to 12

It does not yield any characteristic colour reactions by which it can be detected, as does the similar gurun balsam oil, so that the best method for its detection lies in a careful comparison of the physical characters of the various fractions of a genuine and a suspected oil. A pure African copaiba oil, distilled by the writer (E. J. P.) and C. T. Bennett, yielded the following four equal fractions of 25 per cent. each, on distillation:—

	Specific gravity.	Rotation.	Refractive index.
1	0.917	+ 17° 30'	1.5030
2	0.918	+ 28° 30'	1.5043
3	0.921	+ 46°	1.5060
4	0.927	+ 55°	1.5082

Similar results were found with other normal samples of African copaiba oil. Oil of peppermint has been found by the

writer grossly adulterated with this oil. The influence of the adulterant is clearly indicated in the fractionation of the oil, by the entirely abnormal increase in specific gravity, optical rotation to the right, and refractive index of the later fractions of the adulterated oil.

**HAWTHORN PERFUME.**—The basic material used for the manufacture of all hawthorn perfumes is artificial hawthorn, usually known as aubepine (*vide* "Anisic Aldehyde"). Various floral extracts are based upon this to round it off and give it a distinctive odour, according to the individual perfumer's taste. The natural perfume of mayblossom, *Crataegus oxycantha*, is not a commercial article.

**HEDYOSMUM.**—The so-called tobacco bush of Jamaica is *Hedyosmum nutans*. It yields an essential oil which recalls the odour of certain tobaccos, and is said to be of value as a soap perfume. It has so far, however, not appeared on the market as a commercial article.

**HELICHRYSUM OILS.**—Various species of helichrysum, a genus belonging to the natural order *Compositæ*, yield essential oils having an odour value. *Helichrysum saxatile*, according to Francesconi and Sernagiotto (*Gazz. Chim. Ital.*, 44, 1914, ii., 419), yields an oil with an odour recalling that of roses, and having a specific gravity 0.902; optical rotation,  $-11.7^{\circ}$ ; and refractive index, 1.4769. Its constituents are unknown.

*Helichrysum arenarium* yields 0.4 per cent. of essential oil of powerful aromatic odour recalling that of celery. Its specific gravity is 0.921 at  $20^{\circ}$ ; acid value, 14.5; and ester value, 9. It probably contains *para*-cresol. *Helichrysum angustifolium* is a fragrant herb widely distributed in southern Europe. It grows in masses near Genoa, and also in Hungary and Dalmatia. Schimmel & Co. (*Report*, October, 1903, 73; April, 1909, 57; April, 1914, 65) obtained from it 0.075 per cent. of essential oil of specific gravity 0.892 to 0.920; optical rotation,  $+4^{\circ} 25'$  to  $-9^{\circ} 40'$ ; refractive index, 1.4745 to 1.4849; acid number up to 15; and ester value, 39 to 134. The oil is rich in nerol, partly in the free state and partly in the form of esters.

**HELIOTROPIN.**—The perfume of heliotrope, commonly known as "cherry pie," was for many years a great favourite, although it has probably lost its popularity owing to its having been overdone by an indiscreet use of the artificial heliotropin to excess, with the result that many perfumes containing it are so

strong as to be vulgar and objectionable. The ordinary heliotrope plant is a native of Peru, *Heliotropum Peruvianum*, belonging to the natural order *Boraginaceæ*. This plant was introduced into Europe about the middle of the eighteenth century. There are a very large number of species of the genus, which are for the most part highly odorous, and which are found distributed all over the world, especially in tropical and sub-tropical regions. The flowers are treated to a small extent for the natural perfume, and the triple extract, absolute and concrete, are obtainable on the market. The bulk of the heliotrope perfumes sold to the public, however, are either entirely or chiefly based on the artificial heliotropin. This body very faithfully reproduces the odour of the plant, but is rather too crude, and requires "rounding off." This is best achieved by the use of a very small amount of vanillin, together with a very minute quantity of benzaldehyde. Numerous other bodies blend well with heliotropin, but where used to any extent, result, of course, in a fancy perfume in which, *pro tanto*, the heliotropin has lost its characteristic dominating odour.

It was in 1876 that Tiemann and Haarmann, in the course of their researches on the perfume of this plant, recognised that it was in the main due to two bodies, heliotropin and vanillin. Various types of vanilla beans, and also the flower of the meadow-sweet (*Spiræa Ulmaria*), were also found to contain very small quantities of heliotropin. In 1910 Elze found it to be present in the essential oil of *Robinia pseudacacia*, and soon afterwards Dieterich claimed to have detected traces of it in ordinary beeswax. Its occurrence in nature, however, is rare, and wherever it is found it exists in very small quantity, usually in minute traces. It is probably formed in the plant by the decomposition of a glucoside.

To-day the world's supply of heliotropin is derived from oil of camphor, which contains a large quantity of safrol, the raw material which yields heliotropin. Originally, however, artificial heliotropin was made from the alkaloid piperine  $C_{17}H_{19}NO_3$ . Pepper (preferably Singapore pepper), which contains from 7 to 9 per cent. of the alkaloid piperine, is ground to a fine powder and mixed with twice its weight of slaked lime and a little water, and the mixture evaporated to dryness. The dry mass is then extracted with ether, which dissolves the alkaloid, which is left behind on the evaporation of the solvent. The piperine is then boiled for some time with alcoholic potash, by which means it

is converted into potassium piperate. This body is dissolved in fifty times its weight of water, and is then oxidised by means of potassium permanganate. The manganese oxide formed is filtered off and the filtrate evaporated, when the heliotropin crystallises out.

Safrol (*q.v.*) is the odorous constituent of oil of sassafras, but it also exists to a considerable extent in camphor oil, from which it can be obtained considerably cheaper than it can from sassafras oil. In 1890 Eyckmann found that safrol yielded heliotropin, or piperonal as it was then frequently termed, on oxidation. It was also found that the yield was better if isosafrol were used. Ciamician and Silber (*Berichte*, 1890, 23, 1160) found that, if potassium permanganate were used for oxidation, a ketonic derivative was formed which diminished the yield of heliotropin, but that, if bichromate of potash were used, this did not occur.

In the commercial production of heliotropin camphor oil is fractionally distilled on a very large scale, and the safrol so obtained is heated with alcoholic potash, and is thus isomerised to isosafrol in the same way as eugenol is isomerised to isoeugenol for vanillin manufacture. The isosafrol is rectified, and is then oxidised as follows: A mixture of 25 parts of bichromate of potash, 80 parts of water, and 5 parts of sulphuric acid is poured slowly into 5 parts of isosafrol with continual stirring, the temperature not being allowed to rise materially. When the reaction is complete, the reaction mass is steam distilled and the distillate is extracted with ether. On evaporation of the ether, the heliotropin, in an impure condition, is left behind, and is purified by conversion into its sodium bisulphite compound in the usual manner.

Several patents have been taken out for the manufacture of heliotropin by oxidation of isosafrol by means of ozone (*e.g.*, British Patent No. 6593 of 1895). There the oxidising agent is ozonised oxygen, which oxidises the isosafrol, preferably dissolved in acetic acid. When the oxidation is complete, the acetic acid is evaporated *in vacuo* and the heliotropin extracted with ether and purified by means of its bisulphite compound in the usual manner. Heliotropin can also be made by treating protocatechuic aldehyde with methylene iodide in the presence of an alkali. This method, however, is not a commercial one, but has confirmed the constitution of the compound.

Heliotropin is a white crystalline compound melting at 37°.

Its perfume is powerful and very sweet. It is, however, injuriously affected by exposure to a temperature several degrees below its melting point, and it should therefore be stored in a cool place. It is also better to keep it in a dark place, as the effect of strong light appears to be adverse to the keeping properties of heliotropin. Some perfumers always keep heliotropin dissolved in alcohol, ready for use as required, when decomposition is largely obviated. There are many fancy names resembling heliotropin, but most of them merely disguise a mixture of pure heliotropin with a little vanillin or coumarin, and a fancy price is paid for them. The intelligent perfumer will purchase pure heliotropin and do his own blending. The determination of the melting point is the best criterion of the purity of this substance. This should be sharp at 37° to 38°, a gradual melting indicating adulteration. If an exhaustive examination is required, heliotropin may be converted, by excess of bromine in carbon bisulphide, into bromopiperonal  $C_6H_2Br.(CHO)(O_2.CH_2)$ , which forms crystalline needles melting at 129°. It also forms two isomeric oximes, of which one melts at 110° to 112°, and the other at 146°. It yields a semicarbazone melting at 146°, and a nitro-derivative melting at 94° to 95°.

**HELIOTROPYL-ACETONE.**—This body, or piperonyl-acetone, is a crystalline compound melting at 55°, and boiling at 165° at 12 mm. pressure. It has a characteristic and very pleasant floral odour. According to Kaufmann and Radosevic (*Berichte*, 1916, 49, 675) it can be prepared by emulsifying an acetone solution of heliotropin with water and treating the emulsion with a 40 per cent. solution of caustic soda. This results in the formation of piperonal-acetone melting at 107° to 108°. Hydrogen in the presence of colloidal palladium reduces this to piperonyl-acetone.

**HEMEROCALLIS FLAVA.**—This plant is known as the yellow tuberose. Its natural perfume is not obtainable, but an artificial perfume is sometimes made by using terpineol, hydroxycitronellal, amyl salicylate, and similar synthetics. It is not, of course, more than a rough copy of the natural perfume.

**HEPTANE.**—This body is one of the aliphatic or fatty hydrocarbons which are of rare occurrence in essential oils. It is a very volatile liquid of the formula  $C_7H_{16}$ , of specific gravity 0.688, and boiling point 98° to 99°. It has been found in the essential oils of *Pinus Sabiniana*, *Pinus Jeffreyi*, and a few other allied species.

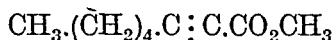
**HEPTINE CARBONATES.**—Heptine  $CH_3(CH_2)_4.C : CH$  is

the parent substance of a new and most important series of artificial perfume materials. Of these amyl-heptene carbonate has already been described. It will here be convenient to deal with the heptene carbonates together with allied acetylenic esters. The chemistry of this important group of bodies is well summarised by Valli-Donan (*American Perfumer*, 1923, 133, and *Rev. de la Parfumerie*, March, 1923, p. 4). He points out that among the constantly increasing number of organic synthetic products which have been found useful in perfumery, methyl heptene carbonate deserves a special place, on account of the unusual interest of its method of manufacture, as well as the remarkable advantages of its use.

The preparation of this ester requires the most painstaking technique and delicate management at the disposal of modern chemistry. Nevertheless, its development from the laboratory to the factory scale has been effected without mishap, the industrial product attaining, from the start, a high degree of perfection.

It was in the course of the research of Moureu and Delange (*Bull. Soc. Chim.*, 1903, 29, 648) that methyl heptene carbonate was discovered, together with numerous other derivatives having the triple bond.

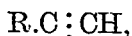
Methyl heptene carbonate



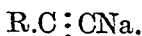
is a colourless liquid, mobile, boiling at  $107^\circ$  at 20 mm. pressure, and having a specific gravity 0.9524. When pure, it has a strong, sharp, penetrating, disagreeable odour. But when sufficiently diluted, it gives off a very fine and very persistent fragrance of fresh violets, which renders it very valuable in the compounding of extracts and original perfume compositions.

In conjunction with the ionones and methyl ionones, it is capable, in some measure, of replacing violet extracts, and of imparting an original note to the perfume bases, more and more complex, used by the perfumer.

If one considers a true acetylenic hydrocarbon of the general formula

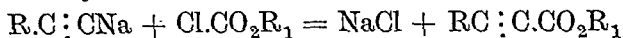


it is clear that the end hydrogen atom, the one which is attached to the carbon atom bearing the triple bond, possesses acid properties, and that it is therefore possible to replace it by a monovalent metal, for example, sodium :



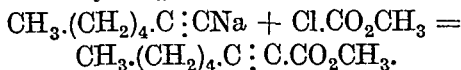
The sodium hydrocarbon compound thus formed is a molecule capable of many reactions, and, in particular, reacting especially easily with halogen derivatives.

If it is treated with a chlorocarbonic ester, there will be formed directly an acetylenic ester :



R and R<sub>1</sub> may be identical or different, aliphatic or cyclic.

In the case of methyl heptine carbonate the equation becomes



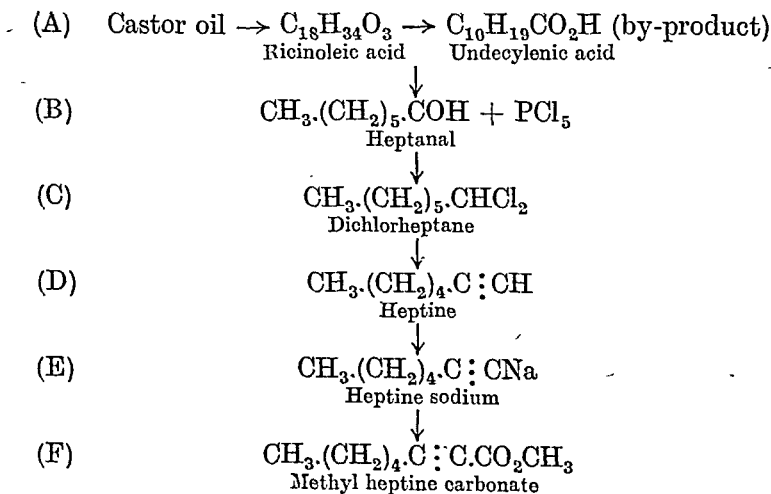
The order of procedure is therefore :—

- (1) The preparation of an acetylenic hydrocarbon.
- (2) The making of its sodium derivative.
- (3) The subjection of this sodium derivative to the action of a chlorocarbonic ester.

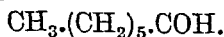
In the preparation of methyl heptine carbonate the starting material is the ricinoleic acid existing in castor oil. When heated, this acid gives an aldehyde containing seven carbon atoms, that is, œnanthol, also called heptanal, which is then to be chlorinated by means of phosphorus pentachloride.

The resulting dichloride, saponified with potassium hydroxide, gives heptine.

It is possible to represent this series of reactions by the following equations :—



#### A. Preparation of Heptanol

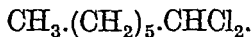


The decomposition of ricinoleic acid is effected by heating crude castor oil (Kraft, *Berichte*, 10, 2034; Erlenmeyer, *Annalen*, 176, 342; Jourdan, *Annalen*, 200, 1020) in a distilling apparatus of enamelled iron, using direct heat at 160° to 170° under a pressure of 100 mm.

The heptanal, which distils off together with a small proportion of water, is fractionated under a pressure of 9 mm. The distilling apparatus should be capacious, for there is considerable foaming.

The yield from this operation is quite small (10 to 12 per cent.), and part of the undecylenic acid becomes polymerised. Haller has suggested that the decomposition be performed not upon ricinoleic acid, but upon its esters.

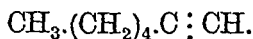
#### B. Preparation of the Dichlor derivative



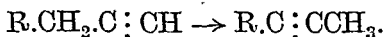
Into a dry vessel provided with a mechanical agitator phosphorus pentachloride is introduced. The vessel and its contents are cooled to - 5° by a refrigerating mixture, the agitator is started, and heptanal is introduced little by little, the temperature being kept below 0°.

After all the heptanal has been added, the temperature is allowed to rise, and the mass is then heated, stirring all the while, until the reaction is completed. It is then cooled and poured carefully into ice water. The oxychloride of phosphorus dissolves and decomposes, while the dichlor-compound formed is separated by decantation, washed until free from acid, dried with anhydrous sodium sulphate, and rectified by vacuum distillation under a pressure of 15 mm. The fraction coming over at 60° to 75° is collected.

#### C. Preparation of Heptine



Originally, the saponification of the dichlor-derivative formed by the preceding operation was effected by the use of alcoholic potash (Béhal, *Bull. Soc. Chim.*, 49, 581, 888), but the yield was unsatisfactory owing to a molecular transformation, which was studied by Faworski (*Berichte*, 20, 781; 21, 1614; Kraft, *Jour. Prakt. Chem.*, 2, 37, p. 420):



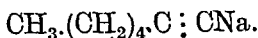
Nowadays, in accordance with the results of Degrez, the saponification is performed by the use of dry pulverised potassium hydroxide, with the aid of heat and at reduced pressure.



The resulting product is poured into ice water, separated, washed, dried carefully over anhydrous sodium sulphate, and rectified in a vacuum. The object of this rectification is to free the heptene from chlorinated ethylenic hydrocarbons which usually accompany it. (A complete separation by rectification is difficult, if not impossible.)

The boiling point of crude heptene is  $100^{\circ}$  to  $106^{\circ}$  at 760 mm.

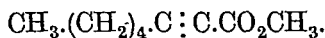
#### D. Preparation of Heptene Sodium



The sodium derivative of the hydrocarbon is obtained by the following method:—

One kilogram of heptene, dissolved in absolutely anhydrous ether, is placed in a reflux apparatus provided with an agitator. There is then introduced, little by little, 240 grams of sodium, in fine wire, in the cold. The reaction, vigorous at first, slows down toward the end, and is brought to completion by gentle heating until the metal disappears.

#### E. Preparation of the Heptene Carbonate



The sodium having been entirely dissolved, a quantity of anhydrous ether is added to the distilling apparatus, so as to provide 10 parts of ether to 1 part of the sodium derivative. While stirring, there is then added, little by little, 9 parts of methyl chlorocarbonate. The mixture is left, while constantly stirring, for several hours, and slight heating is used to complete the reaction. It is then cooled and the product decanted, washed with water, and distilled through a fractionating column under a pressure of 20 mm. The pure product boils at  $107^{\circ}$  under 20 mm.

In general, the homologues of methyl heptene carbonate (*vert de violette*) are prepared by similar methods. This applies to compounds differing with regard either to the acetylenic hydrocarbon from which they are derived or to the radicle which is combined with the acid.

The delicate point in these preparations is the making of the hydrocarbon. The starting material is an aldehyde or a ketone which is easily obtainable, either by synthesis or by some simple chemical process from a natural source.

As examples falling within one or the other of these two classes we may mention methyl isoamyl ketone, which is prepared by the controlled decomposition of ethyl isobutylacetate; methyl hexyl ketone, which is formed by the oxidation of caprylic acid; methyl

# PERFUMERY

heptyl and methyl nonyl ketones, which exist respectively in Algerian and in ordinary commercial oil of rue.

An important source of further compounds is the undecylenic acid which is obtained as a residual by-product in the manufacture of heptanal, the first stage in the preparation of methyl heptene carbonate. This undecylenic acid may be esterified, transformed into an alcohol by the method of Bouvaut and Blanc, and thence into an aldehyde which may serve as raw material for acetylenic derivatives of the same number of carbon atoms.

At the present time certain French houses are marketing the following acetylenic esters :—

Heptene carbonates of methyl and ethyl.

Octene carbonates of methyl, ethyl, and amyl.

Decene carbonates of methyl and ethyl.

Undecene carbonate of methyl.

The following esters of this series are known :—

Hydro-carbon.	Source from which obtained.	Corresponding ester.	Boiling point.
Pentene	Methyl propyl ketone .	Methyl .	126°-127° at 24 mm.
		Ethyl .	93°- 94° „ 24 „
		Isoamyl .	127°-128° „ 22 „
Isopentene.	Isovaleraldehyde .	Methyl .	68°- 69° „ 20 „
		Ethyl .	83°- 84° „ 19 „
		Isobutyl .	99°-101° „ 19 „
Hexene .	Methyl butyl ketone .	Methyl .	91°- 93° „ 19 „
		Ethyl .	106°-108° „ 84 „
Isohexene	Methyl isoamyl ketone .	Methyl .	98°- 99° „ 19 „
		Ethyl .	110°-112° „ 18 „
Heptene .	Ricinoleic acid . . .	Methyl .	107° „ 20 „
		Ethyl .	115°-116° „ 17 „
		Isopropyl	126°-127° „ 20 „
		Isobutyl .	138°-139° „ 23 „
		Isoamyl .	148°-149° „ 20 „
Isoheptene	Methyl isoamyl ketone .	Methyl .	98°- 99° „ 18 „
		Ethyl .	110°-112° „ 18 „
Octene .	Methyl hexyl ketone .	Methyl .	122° „ 19 „
		Ethyl .	126°-128° „ 16 „
		Isopropyl	145°-148° „ 32 „
Isooctene .	Isohexyl methyl ketone	Isoamyl .	168°-172° „ 26 „
		Methyl .	122°-127° „ 31 „
Nonene .	Methylheptenone .	Ethyl .	135°-137° „ 30 „
		Methyl .	133°-135° „ 21 „
Undecene .	Methyl nonyl ketone .	Ethyl .	143°-146° „ 21 „
		Methyl .	168°-172° „ 30 „

**HEPTYL ACETATE.**—This ester has a floral-fruity odour. Its specific gravity is 0.875 ; and boiling point about 192°.

**HEPTYL ALCOHOL.**—This alcohol, also known as *œnanthyl* alcohol, is methyl-amyl-carbinol, of the formula  $\text{CH}_3\text{CH}(\text{OH})\cdot\text{CH}_2\cdot(\text{CH}_2)_3\cdot\text{CH}_3$ . It is a liquid with a powerful aromatic odour, and has been found occurring naturally in oil of cloves. It has a specific gravity about 0.832 at 15°, and boils at 175° to 176°. It can be prepared from the corresponding aldehyde, *œnanthic* aldehyde (heptyl aldehyde), by melting sodium in dry hot toluene, and well stirring until the particles are in a minute state. The mixture is then cooled in ice and the aldehyde dissolved in acetic acid, and toluene is slowly added, with continual stirring. When the reduction is complete, water is added and the toluene layer separated, and the heptyl alcohol purified by fractional distillation. Traces of it are used in artificial carnation perfumes.

**HEPTYL ALDEHYDE.**—See under “Aldehydes, Fatty.”

**HEPTYL FORMATE.**—This ester resembles the acetate. Its specific gravity is 0.884 ; and boiling point about 177°.

**HEPTYL HEPTOATE.**—This ester,  $\text{CH}_3(\text{CH}_2)_5\cdot\text{OOC}\cdot(\text{CH}_2)_5\text{CH}_3$ , is of very powerful fruity odour, and is one of the most expensive of recent additions to synthetic perfumery.

**HEPTYL VALERIANATE.**—This ester has a very fruity odour. Its specific gravity is 0.8775 ; and boiling point about 244°.

**HERABOL MYRRH.**—See “Myrrh.”

**HERABOLENE.**—This body is a tricyclic sesquiterpene found in the essential oil of herabol myrrh. Von Friedrichs (*Arch. der Pharm.*, 1907, 245, 208) found it to have the following characters:—

Boiling point (at 16 mm.)	. . .	130–136°
Specific gravity at 20°	. . .	0.943
Optical rotation	. . .	– 14° 12'
Refractive index	. . .	1.5125

It yields a dihydrochloride melting at 99°.

**HERACLEUM OILS.**—The heracleum oils are of interest in that several of them contain the higher fatty alcohols and their esters, substances which have recently become so important to the up-to-date perfumer. *Heracleum sphondylium* is one of the umbelliferous plants, known as the cow-parsnip. The fruit of

this plant yields from 0.5 to 3 per cent. of essential oil, having the following characters :—

Specific gravity	.	.	.	0.865–0.880
Optical rotation	.	.	.	0° to + 2°
Refractive index	.	.	.	1.4260–1.4330
Acid value	.	.	.	4–16
Ester value	.	.	.	214–276

Zincke (*Annalen*, 1869, 152, 1) found the oil to consist mainly of the caproic and acetic esters of normal octyl alcohol. Moslinger (*Berichte*, 1876, 9, 998) examined two oils in which he found ethyl butyrate; a hexyl ester, probably the acetic ester; octyl esters, including the acetate, caproate, caprinate, and laurate.

Gutzeit (*Annalen*, 1872, 163, 193) has examined the oil of *Heracleum giganteum*, in which he found ethyl butyrate. The oil of the fruits of this plant has been examined by Schimmel & Co. (*Report*, October, 1906, 41; April, 1908, 57) and found to have the following characters :—

Specific gravity	.	.	.	0.8722–0.8738
Optical rotation	.	.	.	+ 1° to + 1° 14'
Refractive index	.	.	.	1.4240
Acid value	.	.	.	1.6–3.7
Ester value	.	.	.	281–288
Ester value (after acetylation)	.	.	.	311–314

**HERNANDIA OIL.**—From the wood of *Hernandia peltata*, a plant known in Madagascar as *faux camphrier*, from 1 to 2 per cent. of an essential oil of powerful cuminal odour has been obtained. It was examined by Semmler and Zaar (*Berichte*, 1911, 44, 815), who found it to contain perillaldehyde (dihydrocuminic aldehyde), myrtenal, cineol, and limonene. Schimmel & Co. have examined the oil from several parts of the plant, with the following results: (*Report*, October, 1914; April, 1915, 51). Four samples of the trunk wood yielded between 1.03 and 2.06 per cent. of oil having the following characters: specific gravity, 0.958 to 0.963; optical rotation, + 83° 45' to + 104° 12'; and refractive index, 1.4969 to 1.5011. Between 75 and 80 per cent. of aldehydes were found in the oil. The root wood yielded 0.5 per cent. of oil which had a specific gravity 0.9667; optical rotation, + 126° 15'; and refractive index, 1.5038. It contained 92.5 per cent. of aldehydes. The oil distilled from the whole fruits (amounting to 0.5 per cent.) had a specific gravity 0.953; optical rotation, + 50° 16'; and refractive index, 1.4955. It contained 49 per cent. of aldehydes. The almond-shaped kernels yielded 1.38 per

cent. of oil, of specific gravity 1.0044; optical rotation,  $+ 87^{\circ}$ ; refractive index, 1.5061; acid number, 7.3; and ester number, 110.4.

**HEXADECYL ALDEHYDE.**—This body is the normal 16 carbon aldehyde of the saturated fatty series, of the formula  $\text{CH}_3(\text{CH}_2)_{14}\text{CHO}$ . It is usually sold as " $\text{C}_{16}$  aldehyde," or as "strawberry aldehyde" on account of its marked odour and flavour of ripe strawberries. It is obtained from the methyl ester of palmitic acid by the same process as is undecylic acid (*q.v.*) from methyl laurate.

**HEXENOL.**—Walbaum (*Jour. Prakt. Chem.*, ii., 96, 1918, 245) has found this alcohol, in the form of its phenylacetic ester, in Japanese oil of peppermint. It is an alcohol, of the formula  $\text{CH}_3\text{CH}_2\text{CH}:\text{CH}(\text{CH}_2)_2\text{OH}$ , and has the following characters: specific gravity, 0.8508; optical rotation,  $- 0^{\circ} 10'$ ; and refractive index, 1.4803. The phenylacetic ester itself,  $\text{C}_{14}\text{H}_{18}\text{O}_2$ , boils at  $299^{\circ}$ , and has a specific gravity 1.000; optical rotation,  $0^{\circ}$ ; and refractive index, 1.4981.

**HEXINE CARBONATES.**—See "Heptene Carbonates."

**HEXYL ACETATE.**—This ester,  $\text{CH}_3(\text{CH}_2)_5\text{OOC}\cdot\text{CH}_3$ , occurs in oil of *Heracleum giganteum*. It is a liquid of fine fruity odour, boiling at  $170^{\circ}$ , and having a specific gravity 0.890 at  $0^{\circ}$ .

**HEXYL ALCOHOL.**—Normal hexyl alcohol  $\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{OH}$  is present in the oils of several species of heracleum, usually in the form of hexyl butyrate. It boils at  $157^{\circ}$ , and has a specific gravity 0.820 at  $20^{\circ}$ . Isohexyl alcohol is present as its angelic acid ester in oil of Roman camomiles. It boils at  $154^{\circ}$ , and has a specific gravity 0.829, and specific rotation  $+ 8.2^{\circ}$ .

**HEXYL BUTYRATE.**—This ester,  $\text{CH}_3(\text{CH}_2)_5\text{OOC}(\text{CH}_2)_2\cdot\text{CH}_3$  resembles the acetic ester, but has a more powerful fruity odour. It is found in several of the heracleum oils, and in the oil of *Theobroma Cacao*.

**HEXYL FORMATE.**—This ester closely resembles heptyl formate. Its specific gravity is 0.888; and boiling point  $154^{\circ}$ .

**HEXYL VALERIANATE.**—This ester closely resembles the corresponding heptyl ester. Its specific gravity is about 0.870; and boiling point  $224^{\circ}$ .

**HEXYLENIC ALDEHYDE.**—See under "Aldehydes, Fatty."

**HIBISCUS ABELMOSCHUS.**—See “Ambrette, Oil of.”

**HINOKI WOOD.**—The Hinoki tree, *Chaemæcyparis obtusata*, grows freely in Japan, and thrives exceptionally well in the mountainous districts of Formosa. The wood yields about 2.4 per cent. of an essential oil with a thujone-like odour. It has a specific gravity 0.882; specific rotation,  $+50.37^\circ$ ; and refractive index, 1.4990 at  $18.5^\circ$ . It contains pinene and cadinene, and a small quantity of odorous oxygenated constituents not yet identified.

**HOMOHELIOTROPIN.**—This substance is not a commercial article, but has been produced in the laboratory as a pale yellow oil of agreeable heliotrope odour. It has a specific gravity 1.265; refractive index, 1.5547 at  $15^\circ$ ; and boils at  $133^\circ$  at 8 mm. pressure. It is prepared by passing ozonised air into a solution of safrol in dry acetic acid, and reducing the ozonide so formed by means of zinc powder (*Jour. Chem. Ind. Japan*, 1922, 25, 1409).

**HOMOLINALYL ACETATE.**—This ester, of the formula,  $C_{11}H_{19}OOC.CH_3$ , is an oil of sweet bergamot odour, boiling at about  $115^\circ$  at 15 mm. It is prepared by the action of homolinalol sodium on acetyl chloride.

**HOMORANTHUS OIL.**—*Homoranthus flavescens* is a shrub growing freely in certain parts of New South Wales. Penfold (*Jour. and Proc. Roy. Soc. of N.S.W.*, lvi., 1923, 197) has investigated its essential oil, which is of particular interest in that it is the only Australian essential oil found, so far, to contain the olefinic terpene, ocimene, which is present to the extent of about 80 per cent. The oil, whose earlier fractions have a powerful odour of bananas, is yielded to the extent of 0.35 to 0.82 per cent. It has the following characters: specific gravity, 0.8206 to 0.8429; optical rotation,  $-1^\circ 75'$  to  $+2^\circ$ ; refractive index, 1.4836 to 1.4873; saponification value, 8 to 45.9; and saponification value after acetylation, 51 to 85.4.

On distillation at 10 mm. three crude oils yielded from 81 to 85 per cent., distilling below  $77^\circ$  at 10 mm., whilst the last two consignments gave 16 to 18 per cent., distilling between  $123^\circ$  and  $142^\circ$  at 10 mm. The first lot gave 11 per cent., distilling between  $72^\circ$  and  $120^\circ$ , 12 per cent. between  $120^\circ$  and  $160^\circ$ , leaving a resinous residue of about 14 per cent., which no doubt partially accounts for the high ester and alcohol numbers.

*Determination of d-a-Pinene.*—Repeated fractional distillation at 20 mm., using a six-disc column, of the portion of oil boiling

below 77° at 10 mm. resulted in the partial separation of a small quantity of dextrorotatory constituent distilling below 70°. It had specific gravity at  $\frac{15^\circ}{15}$ , 0.8313; optical rotation from + 8.7 up to + 14.9°; refractive index at 20°, 1.4746. It consisted of *d*- $\alpha$ -pinene together with ocimene, and readily gave a nitrosochloride, which on purification melted and decomposed at 109°.

*Determination of Ocimene.*—Many repeated fractional distillations conducted at 10 and 20 mm. were made, but it was found extremely difficult to remove the associated dextrorotatory terpene, identified as *d*- $\alpha$ -pinene, despite the high content of the olefinic terpene. The best samples separated possessed the following characters :—

Boiling point at 10 mm.	. . .	67°–68°
Boiling point at 20 mm.	. . .	75°–76°
Specific gravity at $\frac{15^\circ}{15}$	. . .	0.8034
Optical rotation	. . .	0° to + 0.3°
Refractive index at 20°	. . .	1.4857–1.4859

Its identity was established by the following experiments :—

(1) The readiness with which it absorbed oxygen when spread on a watch glass. Instead of volatilising in the manner of a true terpene, it readily yielded a tacky resinous mass, which gave highly refracting emulsions with alcohol or water.

(2) On subjecting a sample of boiling point 74° to 75° at 20 mm. to distillation over sodium at 757 mm., the first drops came over at 172°, one-third of its volume distilling at 173° to 175°, the remaining two-thirds boiling between 175° to 182°, thus showing partial conversion into allo-ocimene.

(3) On reduction with sodium and alcohol, dihydromyrcene was obtained in a moderately pure condition, possessing the following characters: boiling point, 68° at 20 mm.; optically inactive; specific gravity at  $\frac{15^\circ}{15}$ , 0.790; refractive index at 20°, 1.4511.

(4) The bromide of the above dihydromyrcene was prepared by dissolving the hydrocarbon in a mixture of 1 part amyl alcohol and 2 parts ether, as recommended in Parry's "Chemistry of Essential Oils," vol. ii., page 68. On recrystallising from boiling alcohol it melted at 88° to 89°.

*Determination of Sesquiterpene.*—The fractions boiling above

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120° at 10 mm. were redistilled, finally over metallic sodium, but the quantity available did not permit of the isolation of the sesquiterpene in anything like a condition of purity, with the single exception of the last distillation. This was partly accounted for by the presence of resinous bodies in the first two lots, which is evident from the following table :—

	Boiling point.	Specific gravity.	Optical rotation.	Refractive index at 20°.
26/9/21	136° to 140° at 5 mm.	0.9492 (17°)	— 7.3°	1.5008
18/10/21	127° „ 140° at 5 „	0.9333 (18°)	— 1.6°	1.5018
24/8/22	133° „ 135° at 10 „	0.9230 (15°)	— 4.25°	1.5040

The last mentioned is as pure a sample as was possible to be obtained.

*Minor Constituents.*—Small quantities of amyl alcohol and its acetic and butyric acid esters were identified.

**HONEYSUCKLE.**—The woodbine, of which there are numerous species, is *Lonicera Periclymenum* (or other species), belonging to the natural order *Caprifoliaceæ*. It is a favourite climber, whose flowers have a delightful fragrance. According to D. McDonald (“Fragrant Flowers and Leaves,” 1895, 71) the following are the principal species of *Lonicera* with fragrant flowers :—

*L. periclymenum*, with large creamy flowers, blooming early in the year, and with a perfume which is most noticeable in the early evening.

*L. serotinum*.—This has reddish flowers, blooming late in summer and in autumn.

*L. caprifolium*.—This is so called because goats are said to be fond of its leaves.

*L. fragrantissima*.—This plant bears fine white, fragrant flowers about February.

*L. brachypoda*.—This is known as Chinese honeysuckle. It bears yellow flowers from May to October.

*L. sempervivens*.—This is a cultivated ornamental climber known as trumpet honeysuckle.

It is very rare that any preparation of honeysuckle flowers is to be found on the market. The fancy perfumes sold under the name honeysuckle are entirely artificial, and do not actually reproduce the natural odour. *para*-Cresol derivatives, phenyl-



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acetic aldehyde, linalol, geraniol, storax, and similar mixtures are used, to which a floral note is given by the addition of a little true flower oil, such as jasmine, etc.

**HOPS.**—The hop is *Humulus lupulus*, one of the *Cannabaceæ*. It and its essential oil are used principally for flavouring purposes, but very small quantities are occasionally used where a special "note" in a perfume is required. Hops, which are themselves fairly expensive, only yield from 0.3 to 1 per cent. of essential oil, which is very costly. It contains a sesquiterpene which Chapman (*Jour. Chem. Soc.*, 1903, 83, 505; 1895, 67, 54 and 780) considers to be a new body and which he termed humulene, but which Deussen (*Jour. Prakt. Chem.*, 1911, ii., 83, 483) considers to be a mixture of the isomeric caryophyllenes. Rabak (*Jour. Agricult. Research Dept. of Agriculture, Washington*, 1914, 2, 115) has also isolated formic, valerianic, and heptylic acids in the free state, and formic, acetic, octylic, nonylic, decylic, cenanthylic, and butyric acids in the form of esters. Myrcenol and its esters are also present. Rabak (*loc. cit.*) gives the following as the characters of pure hop oils of various origins :—

Origin.	Year.	Yield per cent.	Specific gravity.	Refractive index.	Acid no.	Ester no.	Solubility in 94 per cent. alcohol.
California .	1907	0.24	0.823	1.4856	2.3	44.4	5.4 vol.
	1908	0.35	0.836	1.4738	1.7	45.5	4 "
	1909	0.38	0.839	1.4730	1.8	46.8	3.6 "
Oregon .	1907	0.20	0.8343	1.4802	1.6	57.0	4.6 "
	1908	0.32	0.838	1.4730	1.0	50.2	3.3 "
	1909	0.30	0.8433	1.4705	2.8	56.0	3 "
New York .	1907	0.16	0.862	1.4804	3.6	61.0	3.5 "
	1908	0.14	0.837	1.4756	2.1	47.0	3.5 "
	1909	0.15	0.8777	1.4800	2.5	51.8	3.7 "
Washington .	1908	0.36	0.850	1.4763	1.0	51.8	3.5 "
	1909	0.38	0.8464	1.4734	1.5	53.8	3.3 "
Saaz (Bohemia)	1907	0.32	0.855	1.4905	1.5	52.8	4 "
	1908	0.23	0.824	1.4852	1.0	52.8	6 "
	1909	0.24	0.861	1.4829	3.0	55.3	4 "

**HOUND'S TONGUE.**—This is the popular name for *Liatris odoratissima*, an odorous plant whose leaves contain coumarin, growing in the savannahs of North Carolina to Florida. (See "*Liatris odoratissima*." )

**HOUTTUYNIA GORDATA.**—This plant is known in Japan as *Dokudame*, and, according to Shinosaki (*Jour. Chem. Ind. Japan*, 1921, 24, 557), the whole herb yields, on distillation, 0.005 per cent. of a brownish essential oil having a specific gravity 0.8744; specific rotation,  $-5^{\circ}$ ; refractive index, 1.4685; acid number, 16.65; and saponification number, 28.4. It contains methyl-nonyl-ketone and an aliphatic terpene, which is probably myrcene.

**HUMULENE.**—This sesquiterpene (*vide* "Hops"), which may be identical with caryophyllene, was isolated from oil of hops by Chapman (*Jour. Chem. Soc.*, 1895, 67; 54, 780). It is an oil of specific gravity 0.900 at  $20^{\circ}$ , and boils at  $263^{\circ}$  to  $266^{\circ}$ . Deussen considers that this sesquiterpene is identical with caryophyllene (*Jour. Prakt. Chem.*, 2, 83, 483).

**HYACINTH.**—The hyacinth, *Hyacinthus orientalis*, belonging to the natural order *Liliaceæ*, is a native of Syria and other districts of western Asia. According to Poucher ("Perfumes and Cosmetics," p. 222), it was introduced into Great Britain during the sixteenth century. It was then only a single-flowered plant, but during the seventeenth century double-flowered plants began to appear. The plant is to-day cultivated on a large scale in Holland, particularly in the neighbourhood of Haarlem, which is one of the principal centres of the Dutch bulb growing industry. The odour of hyacinths is sweet and heavy, and if in a confined space, often overpowering. The natural perfume is available in the form of a concrete or an absolute, but the essential oil is not a commercial article (see *P. & E. O. R.*, 1912, 77). The perfumes of different varieties of the flower vary considerably amongst themselves, some types having a rather unpleasant odour. Generally speaking, the odour of the paler-coloured flowers is more delicate than that of the darker varieties, and single flowers usually give a better yield of concrete essence than double ones.

Enklaar (*Chem. Weekblad*, 1910, 1) obtained a small amount of the essential oil by extracting the flowers with benzene, distilling off the solvent at low pressure, precipitating waxy matter with dilute alcohol, and again distilling. The yield was only 0.016 per cent. of the weight of the flowers. The oil itself is of rather unpleasant odour until heavily diluted. On washing it with dilute alkaline solution, traces of sulphuretted hydrogen were removed from it. The oil was fractioned at 10 mm. pressure and

separated into three fractions : (1) boiling below  $90^{\circ}$ , (2) boiling between  $92^{\circ}$  and  $94^{\circ}$ , and (3) boiling from  $94^{\circ}$  to  $150^{\circ}$ .

The first fraction was found to contain a very volatile substance of disagreeable odour, which has not been identified. In the second fraction a body was found, possibly of the formula  $C_{15}H_{20}O$ , having the following characters : specific gravity, 0.907 ; refractive index, 1.4914 at  $16^{\circ}$  ; boiling point,  $205^{\circ}$  to  $206^{\circ}$  ( $92^{\circ}$  to  $94^{\circ}$  at 10 mm.) ; and optical rotation,  $+1^{\circ} 52'$ . Fraction (3) was found to contain benzyl benzoate, and probably free benzyl alcohol and cinnamic acid esters. Traces of vanillin and free benzoic acid are also probably present. A fluorescent basic substance, free from nitrogen, was found, but methyl anthranilate was absent. The oil contains about 20 per cent. of esters, 1 per cent. of free alcohols (benzyl alcohol ?), and 5 per cent. of the fluorescent substance mentioned above.

The majority of the perfumes sold under the name hyacinth to-day are either entirely or almost entirely artificial. Into most of them several constituents usually enter. Nearly all of them contain a little terpineol (*q.v.*). The following compounds are also largely employed :—

*α*-Phenylchloroethylene and *α*-phenyl-bromethylene (bromostyrolene) are prepared from cinnamic acid. The former was first prepared by Stenhouse by distilling cinnamic acid with bleaching powder solution. It is formed by passing chlorine into a solution of cinnamic acid in carbon disulphide and decomposing the phenyl-dichloro-propionic acid thus formed by boiling with water. *α*-Phenylchloroethylene boils at  $199^{\circ}$ .

Bromostyrolene or *α*-phenyl-bromethylene is formed when phenyldibromopropionic acid is boiled with water. This acid is prepared by dissolving cinnamic acid in carbon disulphide and gradually adding a solution of bromine in carbon disulphide. It crystallises in plates melting at  $195^{\circ}$ . On boiling with water, *ω*-bromostyrolene is formed, which boils at  $219^{\circ}$  to  $221^{\circ}$  and melts at  $7^{\circ}$ .

Cinnamic alcohol, formerly called styron, is found in styrax and balsam of Peru.

It can be prepared by saponifying cinnamyl esters with potash and steam distilling the product. Synthetically it is obtained by reducing cinnamic aldehyde.

It is a crystalline compound when pure, melting at  $33^{\circ}$  and boiling at  $258^{\circ}$  ; its specific gravity is 1.010 to 1.030 at  $35^{\circ}$ . It is soluble in dilute alcohol, and can thus be separated from alcohols

of the geraniol type. On oxidation it yields cinnamic acid melting at  $133^{\circ}$ , and by further oxidation benzoic acid is formed.

Phenylacetaldehyde is the newest, and perhaps the best, of the artificial hyacinth odours. It is prepared by heating phenyl-chlor-lactic acid with alkalis. When pure, it has a specific gravity of 1.085, boils at  $205^{\circ}$  to  $207^{\circ}$ , and has a refractive index of 1.5253.

**HYDROCARBONS, DETERMINATION OF.**—The determination of terpenes and sesquiterpenes in terpeneless oils is a matter of considerable importance, especially in terpeneless lemon and orange oils. The only process which yields at all accurate results is that of Böcker (*Jour. Prakt. Chem.*, 1914, ii., 89, 199). This will be found described under "Lemon Oil."

**HYDROXYCITRONELLAL.**—This recently introduced synthetic perfume is a mixture of at least two bodies, hydroxycitronellal and dihydroxycitronellal. The commercial article has a specific gravity about 0.955, optical rotation about  $+7^{\circ}$ , refractive index about 1.4530, and boils at about  $115^{\circ}$  to  $135^{\circ}$  at 10 mm. It is of great value in all perfumes of the lily type.

**HYDROXYCOUMARIN.**—See "Umbelliferone."

**HYDROXY-METHOXY-CYMENE.**—This phenol,  $C_{11}H_{16}O_2$  (probably), occurs to the extent of 0.2 per cent. in Cyprian origanum oil (Pickles, *Bull. Imp. Inst.*, 1906, 4, 297).

**HYPNONE.**—This is another name for acetophenone (*q.v.*).

**HYPTIS SUAVEOLENS.**—This is an aromatic plant which is found from Mexico to southern Brazil, and also in the Philippine Islands, Java, China, and the East Indies. The leaves, when dried, are sometimes used as an adulterant of patchouli leaves, so that the resulting patchouli oil will be, *pro tanto*, adulterated with the oil of hyptis. According to Bacon (*Philippine Jour. Sc.*, 1909, 4, A, 130), the plant, which is known in the Philippines as *subcabayog*, yields 0.0135 per cent. of a greenish essential oil with an odour of menthol. The natives of Java know the plant as *daon rærækæ atan*. Menthol appears to be the chief odorous constituent of the oil. *Hyptis spicata* yields an oil containing menthone and pulegone (*Schimmel's Report*, April, 1904, 96). *Hyptis Salzmanni* yields an oil of specific gravity 0.904, having a pleasant odour of camomile and balm, and *Hyptis fasciculata* yields one of specific gravity 0.905, having an odour of balm and origanum oils.

**HYSSOP, OIL OF.**—The ordinary hyssop, *Hyssopus*

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*officinalis*, is a labiate plant indigenous to the Mediterranean countries and Central Asia. It grows wild in the hills of Dauphiné and on the plains of Provence. Like lavender, it prefers chalky hills and dry light soil. It is particularly abundant in the *coussous* of La Fossette and Le Retour, where it flowers in September and October, when it is gathered for distillation. It is also found in the Savoy, Le Bugey, Le Cher, and La Nièvre.

The flowers are of a pale colour, varying from blue to white and rose, and are very odorous. Apart from its odour value, hyssop is esteemed for flavouring purposes, and is said to be an ingredient in some of the famous French liqueurs.

Hyssop is easily cultivated, and from 1,500 kg. of the wild herb about 7.5 kg. of essential oil are obtained. This is a pleasantly aromatic liquid with a sweetish odour. Its characters are as follows:—

Specific gravity	. . . . .	0.925–0.945
Optical rotation	. . . . .	— 12° to — 25°
Refractive index	. . . . .	1.4730–1.4860
Acid value	. . . . .	1–2
Ester value	. . . . .	3–16
Ester value after acetylation	. . . . .	35–48

Jeancard and Satie, however (*American Perfumer*, 1909, 4, 84), report on two samples distilled in Cannes from the fresh flowering herb, which had the following characters:—

	1.	2.
Specific gravity	0.9252	0.9262
Optical rotation	+ 1°	— 2° 6'
Acid value	0.8	0.8
Ester value	9.2	11.9
Ester value after acetylation	70	51.1

According to Gildemeister and Köhler (*Wallach-Festschrift Göttingen*, 1909, 414; *Schimmel's Report*, April, 1908, 57; October, 1909, 69), oil of hyssop contains  $\beta$ -pinene, a high-boiling alcohol (boiling point, 221° to 222°), and sesquiterpene derivatives. The most interesting substance present, however, is a body which has been named *l*-pinocamphone, and which has not been found in any other essential oil. This body is present to the extent of about 50 per cent. of the oil. It has the following characters:—

Formula	. . . . .	$C_{10}H_{16}O$
Boiling point	. . . . .	212°–213° at 752 mm.
Specific gravity	. . . . .	0.9662
Optical rotation	. . . . .	— 13° 42'
Refractive index	. . . . .	1.4742

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It forms a semicarbazone melting at 228° to 229°, and a dibromide melting at 93° to 94°. On reduction it yields a crystalline alcohol melting at 218° and having an odour of camphor.

*Agastache pallidiflora*, the so-called Great Hyssop, one of the labiate plants widely distributed throughout the mountainous regions of the Far West and Pacific coast of the United States, yields an essential oil entirely different from true hyssop oil. The following interesting account of this oil is by J. F. Couch. (See *P. & E. O. R.*, 1922, 177.)

The material which was used in the following experiments was obtained at the experiment station of the Bureau of Animal Industry, at Salina, Utah, situated at an altitude of about 8,000 feet, in the Wasatch Range. The attention of the investigator was first directed to this plant by the very intense, fragrant odour which diffuses through the air in its neighbourhood, and he describes his experiments with it in the *American Journal of Pharmacy*. Before the blossoms of the plant have opened the odour noted resembles that of thyme; after blossoming the odour is more like a mixture of thyme and peppermint. The leaves of the plant bruised between the fingers develop a strong thyme odour; the flowering heads subjected to the same treatment yield an intense peppermint odour with a small thyme component. It was therefore thought of interest to investigate the essential oil of this plant as a possible source of thymol or menthol.

Accordingly several collections of flowering heads and of leaves were made and the fresh material was immediately, except for one experiment, subjected to steam distillation. The quantities used and the yields of dry oil were as follows:—

			Per cent.
July 28.	3,720 grams flowers yielded	6.84 grams oil	. 0.184
Aug. 5.	2,560 grams flowers yielded	3.96 grams oil	. 0.155
Aug. 11.	3,500 grams flowers yielded	11.06 grams oil	. 0.316
Aug. 17.	950 grams leaves yielded	0.79 gram oil	. 0.083

The first flowers collected were just beginning to open, and full maturity was not attained until about two weeks after, when the third lot was collected. This probably accounts for the larger yield of oil from the lot of August 11th. The lot of August 5th was ground through a meat chopper and allowed to stand overnight before distilling. Contact with the air turned the ground material deep brown, possibly through oxidation of some phenolic constituent. The leaves used were carefully separated from the

stems of the plant. These stems are coarse and fibrous, and do not appear to contain oil. The leaves were then ground through the meat chopper and steam distilled.

The oils obtained from the flowers all carried a very penetrating peppermint odour with some marked suggestion of thyme. They were slightly yellow. The oil from the leaves had a rank thyme odour only. None of the samples of oil, nor any of the aqueous distillates containing dissolved oil, affected ferric chloride solution and all were neutral to litmus.

The following physical constants were determined for the oil from the flowers :—

Density at 20°	0.91924
Specific rotatory power at 25°	— 8.60°
Index of refraction at 25°	1.4865

The oil is soluble in the ordinary solvents. On cooling to — 10° and letting stand at that temperature for several hours there was no separation of any crystalline material. Consequently, the amount of free menthol, if any, present cannot be very large. Phenols were tested for by the usual absorption method, using 5 per cent. NaOH. The volume of the oil diminished slightly, but on acidifying and shaking out the aqueous layer with ether, no phenols were found. Pulegone and other ketones were tested for and found absent.

**IANTHONE.**—Ianthone,  $C_{16}H_{24}O$ , is a ketone of the ionone type, resulting from the condensation of citral with mesityl oxide. It has a strong violet odour, resembling that of ionone. It boils at 161° at 10 mm. pressure.

The pseudo-ianthone produced in the condensation is an oil having but little odour of violets, boiling at 180° to 185° at 10 mm. This is isomerised to ianthone by dilute sulphuric acid.

**IDENTIFICATION METHODS FOR PERFUME CONSTITUENTS.**—It frequently becomes of importance to the perfumer to examine compounded perfume materials in order to obtain as much information as possible in regard to their composition. Examinations of this nature require a very considerable amount of skilled knowledge and experience, and are often of the nature of a prolonged research. The separation of constituents in a mixture of, for example, natural isolates and synthetic perfumes may often be effected by physical methods, so that the determination of the usual constants of the separated constituent

may be sufficient to enable an identification to be made. But it is very often necessary to convert the separated constituent into one or more of its crystalline compounds, the melting point of which enables the original substance to be identified with practical certainty.

The following are examples of typical methods for preparing such crystalline compounds :—

(1) *Hydrocarbon Constituents*.—A number of the terpenes form characteristic crystalline derivatives, such as the nitrosochlorides, the bromides, and other compounds.

To prepare the nitrosochlorides, the terpene, or a fraction rich in the terpene, is dissolved in three times its volume of petroleum ether and cooled to 0°. An 8 per cent. solution of nitrosyl chloride, in equal volumes of chloroform and petroleum ether, is gradually added with constant stirring, care being taken that the temperature does not rise much above 0°. Alcohol is then added, and the crystalline precipitate is separated and recrystallised from warm chloroform. Or 5 parts of the terpene, 7 of amyl nitrite, and 12 of glacial acetic acid are mixed at a temperature of 0° or lower, and a mixture of 6 parts of hydrochloric acid and 6 parts of glacial acetic acid, also cooled to 0°, gradually added with constant stirring. Five parts of alcohol are then added, and the mixture is allowed to stand in ice and salt for a time, when a crystalline mass separates out. This is purified by separation, washing with alcohol, drying, and recrystallising from chloroform or ether, as may be necessary.

The bromides of unsaturated terpenes are prepared, *e.g.*, in the following manner. The terpene or terpene fraction is dissolved in four times its volume of glacial acetic acid, and the mixture cooled in ice. Bromine is then added, drop by drop, so long as it becomes immediately decolourised. The mixture is allowed to stand until crystals separate. These are filtered off, dried on porous paper, and recrystallised from acetic ether.

(2) *Alcohols*.—The most important crystalline derivatives which serve for the identification of alcohols are the phenyl-urethanes and the acid phthalic esters. (See also under "Alcohols.")

To prepare the phenyl-urethanes the following method may be used. The alcohol is mixed with 80 per cent. of its weight of phenyl isocyanate, and allowed to stand in a cold place until crystallisation has taken place. The crystalline mass is pressed between porous paper and recrystallised from petroleum ether or ether, as may be necessary.



The acid phthalic esters may be prepared by mixing the alcohol with about an equal weight of phthalic anhydride and half its weight of dry benzene, and heating the mixture under a reflux condenser until it becomes homogeneous. This operation should proceed for an hour, the temperature being slowly increased up to 180° to 190°.

When the mixture is cold, it is shaken with water and dilute solution of caustic soda added until it is very faintly alkaline, using phenolphthalein as indicator. The mixture is then extracted twice with ether, acidified with dilute sulphuric acid, and the solid ester filtered off, dried, and recrystallised from dry benzene.

(3) *Aldehydes and Ketones*.—The oximes, semicarbazones, and phenyl-hydrazones are the most frequently prepared crystalline compounds of the aldehydes and ketones. For the preparation of the oximes equimolecular quantities of the aldehyde and hydroxylamine are heated in alcoholic solution on a water bath for an hour under a reflux condenser. The hydroxylamine is usually added in the form of its hydrochloride, and liberated by means of alkali. For example, 20 grams of camphor are dissolved in 50 c.c. of 95 per cent. alcohol, and 15 grams of hydroxylamine hydrochloride added, and then 15 grams of sodium bicarbonate. The mixture is heated under a reflux condenser for one to two hours, and cooled, diluted with water, and the oxime thus precipitated collected, dried, and recrystallised from petroleum ether.

The semicarbazones are usually obtained by dissolving the aldehyde or ketone in alcohol and adding an equimolecular mixture of semicarbazide hydrochloride and acetate of sodium. The mixture is allowed to stand for a time with occasional shaking, and the semicarbazone is precipitated with water. It is then recrystallised from hot methyl alcohol.

The phenylhydrazones are usually prepared by acting on the aldehyde or ketone with a dilute solution of phenylhydrazine in acetic acid. For example, 10 parts of freshly prepared phenylhydrazine are dissolved in 5 parts of acetic acid, 1 part of the aldehyde added, and the whole heated on a water bath for half an hour. The mixture is allowed to stand for twelve to twenty-four hours, when the precipitate is filtered off, dried, and recrystallised from benzene.

For a number of other useful compounds for identification purposes and their preparation, see "The Analysis of Perfumery and Flavouring Synthetics and Isolates," by T. H. Durrans (*P. & E. O. R.*, 1924, 219).

**IDESIA.**—*Idesia Polycarpa*, also known as *Polycarpa Maximowiczii*, is a large-growing Japanese tree belonging to the *Bixineæ*, bearing highly odorous flowers, which are used locally for perfume purposes, although the perfume is not extracted from them. Their odour is somewhat heavy, but exceedingly sweet.

**ILLURIN BALSAM.**—See “*Hardwickia Balsam*.”

**IMPERATORIA OSTRUTHIUM, OIL OF.**—This oil is distilled from the root of the plant, which is also known as masterwort. It is a plant indigenous to the mountainous regions of central and southern Europe. The yield is about 1 per cent. of an oil of characteristic aromatic odour, and having a specific gravity 0.876; optical rotation,  $+66^{\circ}$ ; and boiling at from  $170^{\circ}$  to  $190^{\circ}$ . Lange (“*Year Book of Pharmacy*,” 1912, 100) has examined an oil distilled from two-year-old Tyrolese plants, which yielded 1 per cent. of essential oil. This oil had the following characters :—

Specific gravity	. . . . .	0.8627 at $20^{\circ}$
Optical rotation	. . . . .	$+59^{\circ} 30'$
Acid value	. . . . .	0.8
Ester value	. . . . .	17.9
Ester value after acetylation	. . . . .	28.4

Esters of isobutyric, isovalerianic, isopropylidene-acetic, formic and acetic acids were present, together with terpenes, and sesquiterpenes.

**INCENSE.**—This substance, used for ecclesiastical purposes, is a perfume material of considerable antiquity. According to Exodus xxx., 34–36, the formula for the substance used in the time of Moses for Jewish ceremonial purposes is as follows : “Take unto thee sweet spices, stacte, and onycha, and galbanum, these sweet spices, with pure frankincense : of each shall there be a like weight : And thou shalt make it a perfume, a confection after the art of the apothecary, tempered together, pure and holy : And thou shalt beat some of it very small and put of it before the testimony in the tabernacle of the congregation.” According to “*Pharmaceutical Formulas*” (8th ed., p. 228), all these constituents are known with the exception of onycha. A lengthy correspondence in the *Chemist and Druggist*, August 26th, 1899, and following issues showed that in the Hebrew it seems almost conclusive that onycha denotes the crustaceous covering of the shells of certain species of univalve shell fish found in the Red Sea and the Indian Sea ; but there are also reasons for supposing that a high grade

gum benzoin was the substance in question. E. M. Holmes stated that a Jewish recipe for the incense used before the destruction of the Temple (incense not now being used in Jewish ceremonial) included as the chief ingredients, balm, onycha, galbanum, frankincense, and in lesser quantities, myrrh, cassia, spikenard, saffron, costus, canella, cinnamon, soap of Carsina, and "a herb fitted to raise a fume." The onycha was to be refined by means of the soap of Carsina, and rendered more powerful by digestion in wine of Cyprus. It is therefore quite apparent that the exact composition of the Levitical incense is unknown, but the following are average specimens of the incense used by the Roman and Anglican churches:—

	Drachms.		Drachms.
Olibanum . . .	16	Olibanum . . .	20
Benzoin . . .	1½	Benzoin . . .	6
Cascarilla bark . .	1	Cascarilla bark . .	5
Storax . . .	½	Cassia bark . .	2
		Cloves . . .	2

The principal gum resin used as the basis of incense is olibanum, or frankincense. (See under "Boswellia Resins.") In addition to this substance, African bdellium is known as African incense. (See under "Bdellium.") African bdellium is mostly derived from *Commiphora africana*. The tree flourishes in the grassy plains of Abyssinia and the Sudan, and is known to the natives as *Oanka*. According to Rançon (*La Parfumerie Moderne*, 1923, 103) the bdellium is gathered from December to May. The natives make eight or ten incisions in the trunk of the tree, and the white liquid which exudes soon turns yellow, and dries in the form of small tears. They are then detached with a metal instrument, softened by exposure to the sun, and the *débris* picked out. A third gum resin, which is known as incense gum, is the so-called incense of India, which is the product of *Boswellia serrata*. (See "Boswellia Resin."). The incense gum described by Avicenne under the name *Koondar* is sold in the bazaars of the Bombay Presidency under the names *Dup Salai* or *Gunda biroza*.

The true "incense," the incense of Arabia, or olibanum, although obtained in the main from *Boswellia Carterii*, also contains the product of other species. According to Birdwood and Flückiger, three varieties are to be distinguished. Of these "Luban Bedowi" or "Luban Makur" is the product of *Boswellia Carterii*, and is known to the natives as "Mohr meddu" (male frankincense; *Mohr Madow*, *Luban Dakar*—see under "Boswellia

Resin"). "Luban Sheheri" is the product of *Boswellia Bhan-Dajiana*, and is the "Mohr add" of the natives. And, lastly, "Luban Mati" or "Luban Meyeti" is the product of *Boswellia Freearana*, and is also known as *female frankincense*.

These native names must be accepted with some caution, as they are often applied loosely to products whose origin is not positively known to the natives.

In the Antilles and in Guiana exudations from forest trees, such as *Protium heptaphyllum*, belonging to the natural order *Burseraceæ*, are known as incense, but these appear to be elemi or tacamahac resins. The white incense is produced by *Protium heptaphyllum* and *Protium altissimum*, whilst the so-called Cayenne incense is produced by *Protium guianense*. On the west coast of Africa several species of *Daniellia*, giant trees of the *Leguminosæ*, are known as incense trees.

**INCHI GRASS OIL.**—The Indian grass *Cymbopogon cæsius* is closely related to *Cymbopogon Martini*, but is undoubtedly a different grass. Where the two grasses meet, transition forms occur. The essential oil had not been carefully investigated until 1922, and as the grass is common in certain districts of India and the essential oil is highly odorous, resembling palmarosa oil, it is possible that it may soon become of commercial importance. The following interesting account of the grass and oil is due to Moudgill and Krishna Iyer (see *P. & E. O. R.*, 1922, 292), and is reproduced fully, as it has not yet appeared in any text-book:—

*Inchippul* or *Sukkumarippul* is the vernacular name by which the botanical species *Cymbopogon cæsius* of Stapf is known in South Travancore. The grass grows wild in profusion on the dry hill slopes, and the leaves, when rubbed, give a pleasant aroma of ginger. Hence the name *inchippul* (gingergrass). The shoots appear early after the rains in June, and the grass flowers between October and January, when it attains a height of 6 feet or more. It then dries up and is invariably destroyed by fire. It may be mentioned that the grass occurs in two varieties, one white and the other red. The white variety alone was used in this investigation. It has been observed that the same grass growing in moist places or in waterlogged tracts is almost odourless; presumably the proportion of essential oil to which the fine aroma is due decreases in wet lands.

The existence of an essential oil in this grass seems to have been well known; but the distillation of this grass for its oil,

reported to have been in practice in former years, has now been entirely given up. Mention is made of this oil by Parry ("Chemistry of Essential Oils and Artificial Perfumes," 1921, vol. i., p. 63) as having been distilled at Arni, in the Madras Presidency, but he adds that no data are available about the properties of the oil.

A sample of the oil distilled from this grass in 1920 was submitted by the Department of Industries, Travancore, for analysis to Dr. Sudborough, of the Indian Institute of Science, Bangalore, and also to the Imperial Institute, London. From a study of the constants of the oil Dr. Sudborough (private report) arrived at the conclusion that it was not identical with any known variety. The attention of the authors was drawn to this by Mr. I. C. Chacko, in charge of the Industries Department, Travancore. At his request a more complete investigation was undertaken, particularly with a view to finding out its value as a perfume oil. While this paper was in manuscript, a similar report was received from the Director of the Imperial Institute, London, who stated that the "inchi" grass oil differs in its constants from all the grass oils of commerce, and that it might be employed as a substitute for palmarosa oil, which it resembles in odour.

Our investigation has shown that this oil is quite different in character from the oils yielded by the closely allied varieties *Cymbopogon flexuosus* (Cochin lemongrass) and *Cymbopogon Martini* (the "motia" and "sofia" grasses of western India). Both these oils are well known in commerce. Citral and geraniol, the valuable constituents of the former and latter oil respectively, are both absent in this oil; while borneol, which has not been reported to be present in either of them, appears to be a characteristic constituent of the oil from "inchi" grass. In addition to *l*-borneol, the oil contains *l*-camphene, *l*-limonene, *l*-terpineol, and sesquiterpene constituents which have not yet been identified.

Six hundred pounds of grass consisting of the upper third of the plant were collected in October, 1921, and distilled in air-dried condition (moisture = 13 per cent.) with steam in a large copper still over a wood fire, the still being provided with a perforated false bottom to separate the grass from the water below, and thus avoid overheating. The yield of the oil was 0.8 per cent. (It may be mentioned that this still, when used for distilling lemongrass, does not compare favourably as regards yield with the so-called country still, which is invariably employed for lemongrass distillation. Therefore it is believed that the above yield for "inchi"

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	From the whole plant.			From leaves only.	From flowers only.	From leaves and flowers.
	Imperial Institute.	Sudborough.	Authors.			
Yield per cent.	—	—	0.8	0.65	1.5	0.85
Solubility in 70 per cent. alcohol	insol.	insol.	insol.	insol.	insol.	insol.
Solubility in 80 per cent. alcohol	—	—	7 vols.	—	—	—
Solubility in 87 per cent. alcohol	—	—	0.8 vol.	{ 0.9 (a) 1.5 vol. }	1 vol.	{ 0.9 (a) 1.1 vol. }
Density $\frac{30^\circ}{4^\circ}$	$15^\circ = 0.9240$ $15^\circ$	$15^\circ = 0.9200$ $15^\circ$	0.9187	0.9056	0.9380	0.9250
Refractive index $n_D$ , $30^\circ$	1.486	1.4849	1.484	1.484	1.495	1.491
Rotation (a), $30^\circ$	— $39^\circ.84$	— $40^\circ$	— $38^\circ.9$	— $42^\circ.5$	— $37^\circ.5$	— $22^\circ.9$
Acid value	1.0	0.03	1.7	1.8	0.4	1.8
Saponification value	7.1	5.9	5.6	6.8	6.1	7.2
Acetyl value (b)	100	98.4	120	100	78.0	89.0
Percentage of aldehydes by weight (Bennett's hydroxylamine method)	4.0	3.0	4.2	5.4	4.1	4.4

(a) The oil is found soluble in 87 per cent. alcohol, but on addition of more alcohol turbidity reappears after a limit indicated by the higher figure.

(b) The difference in acetyl values obtained by other investigators and ourselves is due to the fact that the standard conditions of saponification were modified by us as required by the presence of terpineol.

(c) Percentage of aldehyde determined by the neutral sulphite method.

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grass, considerable though it is for a grass of this nature, may be improved by the use of a proper still under different conditions.) The oil, when freshly distilled from the grass, has a light greenish-yellow colour, which alters to light brown on keeping.

The constants of different samples of oil obtained from different parts of the plant collected at different stages of its growth have been determined, and the results tabulated for comparison. From these figures it would appear that the plant contains a higher percentage of alcohol in an earlier stage of growth, and that the flowers yield a larger percentage of heavier oil, the higher density being due to the presence of a greater proportion of the sesquiterpene fraction. It is intended to investigate further the conditions of distillation from the point of view of quantity and quality of yield, the number of cuttings which can be taken from the same plant, and the best season for distillation.

*Determination of Acetyl Value.*—The presence of terpineol in the oil found on analysis necessitates an alteration in the usual method of saponification. The following optimum conditions were found for this oil: A mixture of 10 c.c. of the oil, 12 c.c. of acetic anhydride, and 2 grams of anhydrous sodium acetate was boiled gently on a sand bath for  $1\frac{1}{2}$  hours. The acetylated oil was washed and dried, and about 3 grams of it saponified by heating on a water bath for 2 hours with 15 c.c. of N/2 alcoholic potash solution.

*Fractionation.*—The oil was fractionated under reduced pressure (11 to 13 mm.), and the following fractions obtained:—

	Boiling point.	Colour.	Percentage by volume.
1.	55°–90°	Colourless . . .	30.0
2.	90°–135°	Light yellow . . .	36.5
3.	135°–160°	Greenish yellow . .	30.0
4.	Residue	Pitch-like . . .	3.5
			(by difference)

The second fraction when cooled gave a large quantity of crystals possessing a camphor-like odour. These were separated by repeated fractionation and cooling.

*Fraction 1.*—This fraction was refractoriated several times under ordinary pressure, and finally about equal quantities of the

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fractions A and B were obtained. As the table shows, A resembles camphene and B resembles limonene :—

	A.	<i>l</i> -Camphene.	B.	<i>l</i> -Limonene.
Boiling point . . .	160°-161°	159°-161°	175.5°-177°	175°-176°
Refractive index . .	1.4540	1.4550	1.4720	1.4746
$[a]_D^{30^\circ}$ . . . . .	—88.1	—104	—80.8	—105
$d_{4^\circ}^{30^\circ}$ . . . . .	0.8584	0.8555 at 40°	0.8490	0.8472

A was definitely identified to be *l*-camphene by preparing its hydrochloride, and also by converting it into isoborneol in the usual way. An attempt to obtain the solid hydrocarbon succeeded only partially. An attempt was made to prepare a solid hydrochloride from B, but it did not succeed. A tetrabromide was, however, obtained and identified as *l*-limonene tetrabromide.

*Fraction 2. Identification of the Solid.*—It was crystallised several times from petrol and found to melt at 203° to 204°. It was identified as borneol by the melting point, boiling point, specific rotation, the chloral compound, its *p*-nitrobenzoate and acid phthalate. Borneol has not been reported to be present in any of the similar *Cymbopogon* oils, and therefore it would seem that the essential oil from *Cymbopogon cæsius* may be characterised by the presence of this alcohol.

*Identification of the Liquid.*—The liquid obtained after the removal of borneol was redistilled under atmospheric pressure with an eight-pear fractionating column, and about 8 per cent. yield (calculated on the original oil) of a colourless sweet-smelling oil possessing the following constants was obtained :—

	Oil.	Terpineol.
Boiling point . . . .	216°-219° ..	217°-218°
$d_{4^\circ}^{30^\circ}$ . . . . .	0.9380 ..	0.933-0.941
$n_D^{30^\circ}$ . . . . .	1.4830 ..	1.4800-1.4840
$[a]_D^{30^\circ}$ . . . . .	—56.4° ..	± 100

The oil was suspected to consist of *l*-terpineol. This was confirmed by the preparation of dipentene dihydriodide from it by shaking with hydriodic acid.

**INDOL.**—This is a substance of considerable value to the perfumer. Closely related to it is the body scatol, and an isomeric methyl-indol, which will be conveniently discussed together with



indol. Although these bodies have very offensive odours in the concentrated form, when they are highly diluted they greatly improve floral odours to which they are adaptable. It is of interest to note that the essential oil of jasmín, when extracted direct from the flowers, contains no indol and no methyl anthranilate. But if the flowers are allowed to macerate in cold fat, so that the life processes are allowed to continue in the tissues, more oil is developed in the flowers, as the original supply passes into the fat. In this further supply of essential oil, both indol and methyl anthranilate appear, so that it is probable that these bodies pre-existed in the form of glucosides, which are broken down in the further biological changes in the plant. The result is that the jasmine perfume obtained by enfleurage is vastly superior in odour to that obtained by extraction with a volatile solvent. It is strange that a substance so objectionable in its natural condition should be of such great value as a perfume material when diluted. It has been discovered in fæces by Brieger (*Jour. Prakt. Chem.*, 2, 17, 133), and in the ordinary digestive products by Nencki and Kühne. It is present in enfleurage oil of jasmine, in neroli oil, clove flower oil, and the oils of *Celtis reticulosa*, *Robinia pseud-acacia*, *Calladium*, *Murraya exotica*, and *Visnea mocanera*. It has also been found in the vapours given off in the extraction of sugar from molasses. In this case it is accompanied by scatol.

Indol  $C_8H_7N$  is the mother substance of the indigo group of compounds, and was discovered by Bayer in 1866 (*Annalen*, 140, 4). Although Lipp was actually the first to synthesise indol, by the condensation of sodium ethylate with amino-chlor-styrolene (*Berichte*, 1884, 17, 1067), the practical development of the chemistry of indol is due almost entirely to Bayer. Indol is a crystalline body melting at  $52^\circ$  and boiling at  $244^\circ$ . It should only be used in minute quantities in floral combinations, as, if used in excess, not only is the perfume ruined, but the indol tends to darken in colour, which under certain circumstances is very objectionable.

Scatol is  $\beta$ -methyl-indol,  $C_8H_6N(CH_3)$ , and is found in ordinary civet and in the essential oil from the wood of *Celtis reticulosa*. It forms white crystals, melting at  $95^\circ$ , and boiling at  $265^\circ$  to  $266^\circ$ . It yields a hydrochloride melting at  $167^\circ$  to  $168^\circ$ , of the formula  $[C_8H_6N(CH_3)]_2HCl$ , and a picric acid compound melting at  $172^\circ$  to  $173^\circ$ . It is equally foul-smelling with indol, and may be used in the same manner, but with even greater caution.

There is an isomeric methyl-indol, known as methyl-indol-2 or methyl-ketol  $C_8H_6N(CH_3)$ . This has been prepared by Fischer by dehydrating the phenyl-hydrazone of acetone by means of zinc chloride at  $180^\circ$ . The reaction is accompanied by the evolution of ammonia. It is a crystalline body melting at  $69^\circ$ , and boiling at  $268^\circ$ , and similar to scatol in its general properties.

Scatol is artificially prepared in a manner similar to that used for the preparation of its isomer. The phenyl-hydrazone of propanal  $C_6H_5.NH.N:CH.CH_2.CH_3$  is dehydrated, preferably by means of cuprous chloride. Arbussow and Tichvinsky (*Berichte*, 1910) obtained a yield of 60 per cent. of the theoretical in this manner. Scatol may be identified by its forming a fine blue colour with a solution of dimethyl-amino-benzaldehyde. There are numerous methods by which indol can be prepared artificially. Most of these, however, are of purely theoretical interest, and only those of some practical importance will be referred to here. To obtain indol naturally, the following process may be used. The essential oil containing it is mixed with 10 per cent. of picric acid and heated to  $60^\circ$ . An excess of petroleum ether is then added. A picric acid compound of indol separates out in long red crystals, which are washed with petroleum ether and decomposed by caustic alkali, the indol thus liberated being dissolved out by extraction with ether, and the residue left on evaporation of the ether is steam distilled, when pure indol passes over. This method is adapted for a fairly accurate quantitative determination. To prepare indol on a satisfactory scale, the following processes may be employed. It is prepared by the reduction of *ortho*-nitro-cinnamic acid by means of zinc dust. It is prepared to a considerable extent as a secondary product during the synthetic manufacture of indigo. If anthranilic acid be treated with monochloroacetic acid, phenyl-glycin-*ortho*-carbonic acid results. By the careful heating of the lime salt of this acid, indoxyl  $C_8H_7NO$  results, which by reduction yields indol. Or anthranilic acid is condensed with hydrocyanic acid and formaldehyde. This results in a nitrile  $C_6H_4(NH.CH_2CN)COOH$ , which on saponification yields the free acid  $C_6H_4(NH.CH_2.COOH)COOH$ , phenyl-glycin-*ortho*-carbonic acid, which is treated as above described.

Other processes which have been recommended for the preparation of indol are those of Berlinerblau (*Monatshefte*, 8, 187); Thiele and Dimiroth (*Berichte*, 1895, 13, 1411); Vorländer-Apelt (*Berichte*, 1904, 1, 1134); Glaud (*Jour. Chem. Soc.*, 1913, 103, 1254), and Weermann (German patent 139822).

Derivative.	Preparation.	Properties.	References.
Indol. . . . .	See above.	Melts at 52°.	See above.
Methyl indol 1 . . .	From methyl indol carboxylic acid	Oil, specific gravity 1.07; boils at 240°	<i>Berichte</i> , 17, 562.
Methyl indol 2 . . .	From $C_6H_4 \begin{smallmatrix} NO_2 \\ \diagup \\ CH_2 \end{smallmatrix} COCH_3$	Melts at 59°; boils at 272°	<i>Berichte</i> , 13, 187.
Methyl indol 3 (scatol) .	Propanal and phenylhydrazine	Melting point, 96°; boils at 266°	<i>Annalen</i> , 236. <i>Berichte</i> , 33, 1404.
Dimethyl indol 1, 2 . .	Acetone and phenylhydrazine	Melts at 86°	<i>Annalen</i> , 236, 153. German Patent 128660.
Dimethyl indol 1, 3 . .	...	Liquid; boils at 240°	<i>Annalen</i> , 236.
Methyl indol b . . .	...	...	<i>Annalen</i> , 236.
Dimethyl indol 2, 3 . .	German patent No. 38784	Melts at 105°-106°; boils at 285°	<i>Annalen</i> 236.
Trimethyl indol 1, 2, 3.	...	Melts at 18°; boils at 282°	<i>Chem. Central.</i> , 27, 81.
Dimethyl indol b, b . .	...	...	<i>Berichte</i> , 35, 2607.
Ethyl indol 1 . . .	...	Boils at 282°	<i>Berichte</i> , 20, 3415.
Methyl ethyl indol 1, 2.	Phenylhydrazine	Melts at 66°	<i>Chem. Central.</i> , 28, 2, 289.

In addition to the colour reaction mentioned above for scatol, the following colour reactions for indol and scatol may be noted. If a few drops of dimethyl-aniline be added to 5 c.c. of a chloroformic solution containing indol, and a little concentrated sulphuric acid be cautiously added, a pale red colour appears at the junction of the liquids, insoluble in chloroform, in the presence of indol; or a violet coloration, soluble in chloroform, in the case of scatol. With citral instead of dimethyl-aniline, there is a yellow coloration with indol, and a red coloration with scatol. These reactions are sensitive to from 1 in 200,000 to 1 in 500,000. Finally, if a few drops of an alcoholic solution of vanillin (5 per cent. strength) are added to a dilute solution of indol or scatol, and the mixture be heated with a slight excess of concentrated hydrochloric acid, an orange-brown colour results in the presence of indol, or a violet colour in the presence of scatol. The useful table of indol derivatives on p. 341 is due to Mirgodin (in *La Parfumerie Moderne*).

**INULA OIL.**—The essential oil of *Inula viscosa* is a pale brown liquid of powerful aromatic odour, recalling hyssop and eucalyptus. It has the following characters :—

Specific gravity	. . . . .	0.9436
Optical rotation	. . . . .	— 24°

*Schimmel & Co. (Report, October, 1903)* have reported on an oil said to be obtained from this plant, but which had characters differing from the above.

This oil had the following characters :—

Specific gravity at 25°	. . . . .	1.006
Acid value	. . . . .	164.6
Ester value	. . . . .	15.8

The plant is widely distributed in Algeria, and is found in the Alpes-Maritimes, and is very abundant in the uncultivated lands of the Maures and the Estérel. The allied plant, *Inula graveolens*, has an odour of lemons. Its characters are as follows :—

Specific gravity	. . . . .	0.9754
Optical rotation	. . . . .	— 36° 40'
Refractive index	. . . . .	1.4759
Acid value	. . . . .	8.45
Ester value	. . . . .	161.3
Ester value after acetylation	. . . . .	239.4

It probably contains bornyl acetate. *Inula Helenium* is Elecampane.

**IONONE.**—The discovery of the original artificial violet perfume is one of the outstanding triumphs of modern chemical research. This body was named ionone by its discoverer, and although to-day there are various allied derivatives, it will be convenient to deal with the whole of the artificial violet compounds under this title.

The perfume of the violet is one of the most popular of the floral odours, but since the actual percentage of odoriferous material is so minute, it has never been possible to isolate sufficient of the essential oil for a proper investigation to be made. So expensive would such an investigation be that Tiemann and Krüger, recognising the similarity between the odours of the violet and of orris root (it will be remembered that the old-fashioned "violet powder" never contained violet perfume, but was merely powdered orris root mixed with starchy matter), decided to carry out an investigation on the odorous substances of orris root in the hopes that the results would lead them to the knowledge of the violet perfume. Whether this has actually been the case no one knows, but the results of their work and its further development by others have been so successful that the artificial violet perfumes available in consequence are accepted as satisfactory, and it is unlikely that the difficulties attending an exhaustive research on the actual violet perfume will be overcome for many years.

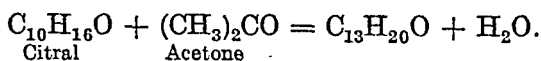
Tiemann and Krüger, whose results were first published in 1893 (*Berichte*, 1893, 26, 2675), worked on orris root, which was extracted with ether, the ether recovered, and the residue steam distilled in order to eliminate the fixed fatty matter, which consists of resins, irigenin, iridic and myristic acids, etc., whilst the volatile portions consist of a little myristic acid and its methyl ester, oleic acid, oleic anhydride, and the characteristic odour bearer, which the discoverers termed irone. It was found that this body was a ketone of the formula  $C_{13}H_{20}O$ . It is an oil which, in the concentrated form, does not resemble violets, but which, on dilution, has a marked resemblance to the violet perfume. Although it is a ketone, it cannot be successfully purified by means of a bisulphite compound. Such methods as using its hydrazone as an intermediary have to be resorted to. Having by a prolonged study of irone and its decomposition products ascertained its constitution, Tiemann and Krüger set out to synthesise it. As a result of these experiments, isomers of irone were obtained, which were at first believed to be but a single body, to which the

name ionone was given. The resolution of this into its isomers followed at a later stage. In the meantime the powerful violet odour of ionone was such as to render it unnecessary, at all events from a commercial point of view, to follow up the irone research, and for the time being the synthesis of irone was not achieved. This, however, has since been achieved, and an interesting paper on the subject was published by Merling and Welde (*Annalen*, 1909, 119) upon the question. Two parts of ethyl acetoacetate and 1 part of acetone are condensed at  $-5^{\circ}$  with the aid of hydrochloric acid. This results in isopropylidene aceto-acetic ester  $(\text{CH}_3)_2\text{C}:\text{C}(\text{COCH}_3).\text{CO}_2.\text{C}_2\text{H}_5$ . This ester is then condensed with the sodium compound of ethyl aceto-acetate (German Patent 148080 of 1902). The chain is thus closed, and the ethyl ester of trimethyl-cyclohexane-carboxylic acid results. To 100 parts of this ester 100 parts of phosphorus pentachloride are added, the temperature being kept very low. The body is thus transformed into the corresponding ester of dichlorocyclogeranic acid, which, by loss of hydrochloric acid, is changed into the ester of the monochlor acid, and this, on reduction by sodium, becomes saturated by taking up 4 atoms of hydrogen, and from this fully saturated compound 1 molecule of hydrogen chloride is abstracted, leaving ethyl- $\Delta$ -4-cyclogeranate.

This ester is decomposed into the free acid, which exists in two stereoisomeric forms, and which, by Merling's process, are converted into the corresponding aldehyde. (For details of this transformation, see "*La technique industrielle des parfums synthétiques*" (Paris, 1923, R. Sornet), pp. 86-87.) Irone results when the aldehyde so prepared,  $\Delta$ -4-cyclocitral, is condensed with acetone. Irone exists in two stereoisomeric forms,  $\alpha$ -irone and  $\beta$ -irone. The mixed body "irone" has a powerful violet odour, and has the following characters:—

Boiling point at 16 mm.	. . . . .	144°
Specific gravity	. . . . .	0.940
Refractive index	. . . . .	1.5011
Optical rotation	. . . . .	about $+40^{\circ}$

Coming back to the initial results of Tiemann, it was found that the substance resulting from the condensation of citral and acetone in the presence of an alkali was not irone, but an isomer having a powerful violet odour (on dilution), which resulted from the following reaction:—



As a result of further researches, this body, which was of a ketonic nature, was named pseudoionone. It was found that, if this body were heated with dilute sulphuric acid and a little glycerine, it was converted into another isomer, to which the name ionone was given. This substance is the original ionone of commerce, which was sold at a fabulous price in a 10 per cent. solution in alcohol. It is now recognised to be a mixture of two isomeric ketones. The complete patent specification for this body, which may be described as epoch making in the art of perfumery, is of sufficient importance to be reproduced textually. It reads as follows:—

"I, J. C. W. F. Tiemann, member of the firm of Haarmann and Reimer, of Holzminden, residing at Berlin, Germany, do hereby declare the nature of this invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement: I have found that a mixture of citral and acetone, if it is subjected in the presence of water for a sufficiently long time to the action of hydrates of alkaline earths, or of hydrates of alkali metals, or of other alkaline agents, is condensed to a ketone of the formula  $C_{13}H_{20}O$ . This substance, which I term 'pseudoionone,' may be produced, for instance, in shaking together for several days equal parts of citral and acetone with a solution of hydrate of barium, and in dissolving the product of this reaction in ether. The residue of the ether solution is fractionally distilled under a reduced pressure and the fraction is collected, which boils at a pressure of 12 mm. at a temperature of from  $138^{\circ}$  to  $155^{\circ}$  C., and from it the unaltered citral and unchanged acetone and volatile products of condensation of acetone by itself are separated in a current of steam, which readily carries off these bodies. The product of condensation remaining in the distilling apparatus is purified by fractional distillation *in vacuo*. Under a pressure of 12 mm. a liquid distils off at a temperature of from  $143^{\circ}$  to  $145^{\circ}$  C. This product of condensation of citral with acetone, which I term pseudoionone, is a ketone readily decomposable by the action of alkalies. Its formula is  $C_{13}H_{20}O$ ; its index of refraction,  $N_d = 1.527$ ; and its specific weight, 0.904. The pseudoionone has a peculiar, but not very pronounced, odour; it does not combine with bisulphite of sodium as most of the ketones of the higher series, but in other respects it possesses the ordinary characteristic properties of the ketones, forming, in

particular, products of condensation with phenylhydrazine, hydroxylamine, and other substituted ammonias. Although the odour of the pseudoionone does not appear to render it of great importance for its direct use in perfumery, it is capable of serving as raw material for the production of perfumes, the pseudoionone being converted by the action of dilute acids into an isomeric ketone, which I term ionone, and which has most valuable properties for perfumery purposes. This conversion may be effected, for example, by heating for several hours in an oil bath 20 parts of pseudoionone with 100 parts of water, 2.5 parts of sulphuric acid, and 100 parts of glycerine to the boiling point of the mixture. The product resulting from this reaction is dissolved in ether; the latter is evaporated and the residue subjected to fractional distillation *in vacuo*. The fraction distilling under a pressure of 12 mm. at a temperature of from 125° to 135° C. is collected. This product may be still further purified by converting it, by means of phenylhydrazine or other substituted ammonias, into a ketone condensation product decomposable under the action of dilute acids. The ketone derivatives of the pseudoionone are converted, under similar conditions, into ketone derivatives of the ionone. The pure ionone corresponds to the formula  $C_{13}H_{20}O$ , it boils under a pressure of 12 mm. at a temperature of about 128° C., its specific weight is 0.935, and its index of refraction is  $N_d = 1.507$ . The ionone has a fresh flower perfume recalling that of violets and vines, and is peculiarly suitable for being used in perfumery, confectionery, and distillery. The ionone, when subjected to a temperature surpassing 100° C. to the action of hydriodic acid, splits off water and gives a hydrocarbon corresponding with the formula  $C_{13}H_{18}$ , boiling under a pressure of 12 mm. at a temperature from 106° to 112° C. This hydrocarbon is converted by strong oxidising agents into an acid of the formula  $C_{12}H_{12}O_6$ , melting at a temperature of 214° C."

Many patents for the production of artificial violet perfume have been taken out since the original patent, but the most important detail in the chemistry of ionone since then is the discovery that commercial ionone is actually a mixture of two isomeric bodies, which have been termed  $\alpha$ -ionone and  $\beta$ -ionone.

Pseudoionone has the following characters:—

Specific gravity at 20°	.	.	.	0.898
Refractive index at 20°	.	.	.	1.53346
Boiling point at 12 mm.	.	.	.	143°–145°



Commercial 100 per cent. ionone has, approximately, the following characters :—

Boiling point at 10 mm. . . . .	126°–128°
Specific gravity at 15° . . . . .	0.935–0.940
Refractive index at 20° . . . . .	1.5035–1.5070
Optical rotation . . . . .	0°

The characteristic odour of this pure (mixed) ionone is that of violets, with a suggestion of the odour of vine leaves and blossoms. Tiemann (*Berichte*, 1898, 31, 808, 867) succeeded in resolving this substance into  $\alpha$ -ionone and  $\beta$ -ionone. By heating pseudo-ionone with dilute sulphuric acid, a different product is obtained from that yielded when strong sulphuric acid is used. In the latter case,  $\beta$ -ionone predominates.  $\alpha$ -Ionone is prepared from the commercial product by converting it into the crystalline oxime, which is recrystallised from petroleum ether, when the ketone can be regenerated by the action of dilute sulphuric acid, when  $\alpha$ -ionone results. This isomer has the following characters :—

Specific gravity at 15° . . . . .	0.934
Refractive index at 20° . . . . .	1.4990
Boiling point at 12 mm. . . . .	127°–128°
Melting point of oxime . . . . .	89°–90°
Melting point of semicarbazone . . . . .	107°
Melting point of bromphenylhydrazone . . . . .	142°–143°

$\beta$ -ionone is obtained from the commercial product by means of the semicarbazone, which crystallises more readily than the corresponding derivative of  $\alpha$ -ionone, and can thus be separated.  $\beta$ -ionone has the following characters :—

Specific gravity at 15° . . . . .	0.949
Boiling point at 12 mm. . . . .	134°–135°
Refractive index at 20° . . . . .	1.5198
Melting point of semicarbazone . . . . .	148°–149°
Melting point of bromphenylhydrazone . . . . .	116°–118°

Lewinsohn (*P. & E. O. R.*, 1923, 259) gives the following account of the modern technical method for the manufacture of ionone :—

Contrary to the descriptions in the patents and sundry publications, the technical preparation of ionone is as follows: The process involves two stages: (a) the condensation of lemongrass oil with acetone to form pseudoionone; (b) the ring-closure or cyclisation of pseudoionone with production of  $\alpha$ - and  $\beta$ -ionones. The German patent (D.R.P. 75120) taken out by Messrs. Haarmann and Reimer of Holzminden for the preparation of ionone claims the condensation of citral with acetone. The modern

practice is to use, in place of citral, the lemongrass oil from which citral is obtained. This makes the process cheaper, and in no way affects the final product.

(a) *Condensation*.—A mixture of equal parts of lemongrass oil, acetone, and 10 per cent. caustic soda solution is stirred for seventy-two hours in an iron stirring vessel, the temperature not being allowed to exceed 35°. (In subsequent batches recovered acetone may be used, but the caustic liquor must be more concentrated to allow for the water contained in the acetone.) At the end of this time the lower aqueous layer is removed, and the upper layer is washed several times with water. From the aqueous layer and washings acetone is recovered by distillation. The reddish brown oily layer is then distilled *in vacuo*. Methylheptenone (formed from the citral) comes over first, and the pseudoionone is collected at 135° to 150° at 5 mm. The yield is almost quantitative, allowing for the fact that lemongrass oil contains only 70 per cent. of citral, a portion of which, as mentioned above, is converted into methylheptenone.

(b) *Cyclisation*.—The cyclisation of pseudoionone requires the greatest care and skill on the part of the operators. According to the concentration of the sulphuric acid used and the temperature of the reaction, varying mixtures of  $\alpha$ - and  $\beta$ -ionones are obtained. Since the former is esteemed more highly and is more valuable than the  $\beta$  compound, the manufacturer must aim at producing the greatest proportion of  $\alpha$ -ionone. The use of an unsuitable dilution of sulphuric acid results in much unchanged pseudoionone and little  $\alpha$ -ionone, the main product being  $\beta$ -ionone. On the other hand, if the concentration of the acid be too high there is formed, together with relatively large amounts of  $\alpha$ -ionone, much resinous residue, and no pseudoionone is recovered. For a maximum yield of  $\alpha$ -ionone, therefore, the strength of the acid must not be increased unduly. The process here described gives a product containing about 90 per cent. of  $\alpha$ - and 10 per cent. of  $\beta$ -ionone.

One part of pseudoionone prepared as above and 3 parts of 60 per cent. sulphuric acid are separately cooled to  $-8^{\circ}$  with continuous stirring. The acid is then allowed to run into the pseudoionone. A rise in temperature is observed. As soon as the thermometer reaches 30° there is seen a sudden change in the dark brown colour, which for some moments becomes clearer. The mixture is now heated as rapidly as possible to 42°, and at once poured upon finely powdered ice. When the ice has melted

the crude ionone floats on the surface as a brown oil. The acid layer is removed, and extracted with benzene. The extract and the crude ionone are united and together washed with water, then with dilute sodium carbonate solution, and finally again with water. The crude product so obtained is distilled *in vacuo*, the water and terpene by-products being removed at 10 to 12 mm., and the ionone itself distilled in a good machine-vacuum at not more than 2 to 3 mm. pressure. At this pressure  $\alpha$ -ionone boils at 118° to 125°,  $\beta$ -ionone at 130° to 135°. With good working there should be no unchanged pseudoionone. When the temperature reaches 135° the distillation is discontinued, and the falling of the mercury in the gauge is the signal for the emptying of the distillation vessel, since the residue quickly sets. With well-trained workers the yield of distilled ionones is about 40 per cent. of the weight of lemongrass oil used, or 70 per cent. on the citral content. The further purification of the ionone so produced (which is itself a commercial article) to give such brands as "ionone extra" and "ionone blanc" necessitates other, somewhat delicate, treatments.

The ionone manufacturer who follows strictly the process described above can be sure of always obtaining a constant product, which, enhanced by the addition of a few drops of "violet green scent" (or, to give it its chemical name, methyl-heptene-carbonate), will find regular purchasers amongst perfumers.

From the above, it is easily understood that pure 100 per cent. ionone may vary considerably according to the exact method of manufacture, and perfumers must judge ionone on its odour, quite apart from its purity. One perfumer may prefer an ionone with less, whilst another prefers more,  $\beta$ -ionone in the product.

It is, moreover, possible to separate the two isomers on a commercial scale. (See especially Tiemann, French Patent No. 229683; and Chuit and Bachofen, *Rev. Chim. pur. et appliqué*, 1903.)

The hydrosulphonic compound of  $\alpha$ -ionone crystallises more readily than the corresponding compound of  $\beta$ -ionone, whilst the latter is the more easily decomposed by a current of steam.

Chuit and Bachofen base their method of separation on the relative insolubility of the sodium salt of the hydrosulphonic compound of  $\alpha$ -ionone in the presence of sodium chloride, whilst the corresponding  $\beta$ -compound remains in solution. If sodium chloride be added to a hot solution of the hydrosulphonic com-

pounds, separation of the  $\alpha$ -salt takes place slowly as the solution cools, and the salt crystallises in fine white scales, which can be recrystallised from hot water. The  $\beta$ -compound remains in solution. From the perfumer's point of view, the complete separation of these isomers enables one to produce numerous shades of violet perfume, since  $\alpha$ -ionone has the sweeter and more penetrating odour, whilst  $\beta$ -ionone, although not so sweet, resembles the true violet flower more completely.

By reducing ionone Skita (*Berichte*, 1912, 45, 3312) has prepared the corresponding dihydroionones, which have odours recalling that of cedarwood. Tiemann, however, has prepared a dihydroionone apparently isomeric with the products of Skita by the condensation of citronellal and acetone. The method is, generally, identical with that employed in the condensation of citral and acetone. Dihydroionone thus produced has a sweet odour of fresh flowers.

A somewhat different shade of odour is produced by the use of homologues of citral for the condensation. Thus, by using methyl-ethyl-ketone—which is a much more difficult and tedious condensation than when acetone is used—a methyl-pseudoionone results which boils at  $160^{\circ}$  to  $175^{\circ}$  at about 20 mm. pressure. By cyclisation as in the case of pseudoionone, it yields methyl-ionone boiling at  $155^{\circ}$  to  $160^{\circ}$  at 24 mm. pressure. Methyl-ionone has an odour somewhat different from that of ionone, and generally regarded as superior to the latter. Durand, Huguenin, and Barbier (French Patent 278338 of September, 1898) have condensed mesityl oxide,  $\text{CH}_3\text{CO}\cdot\text{CH} : \text{C}(\text{CH}_3)(\text{CH}_3)$ , with citral at the ordinary temperature for fifteen hours, with continual agitation, in the presence of caustic soda. This results in the formation of pseudoianthone,  $\text{C}_{16}\text{H}_{24}\text{O}$ , a liquid boiling at  $180^{\circ}$  to  $185^{\circ}$  at 10 mm. pressure. By cyclisation by means of 65 per cent. sulphuric acid in the cold for half an hour, ianthone results. This is a highly odorous liquid boiling at  $161^{\circ}$  at 10 mm. pressure, having a violet odour which differs distinctly from that of ionone.

A body known as cyclo-geraniolidene-acetone has been prepared which is, again, another synthetic violet with a characteristic shade of odour of its own (*Rev. Chem. Ind.*, 1904, 141). If sodium and carbon dioxide be allowed to act on trimethyl-cyclo-hexanone, the corresponding carbonic acid is produced. By the action of reducing agents, this is transformed into trimethyl-oxy-cyclo-hexanone-carbonic acid. If the calcium salt of this acid is distilled with calcium formate, cyclo-geraniolidene-aldehyde,  $\text{C}_{10}\text{H}_{16}\text{O}$ :

results. By condensation with acetone, this yields cyclo-geraniolide-dene-acetone, which is a mixture of two isomers. In practice, this interesting and valuable violet perfume is prepared as follows. Pure ether (4,500 parts) is mixed with sodium (98 parts), and trimethyl-cyclo-hexanone (450 parts) added. The mixture is kept under a reflux condenser, and when the sodium is dissolved a current of  $\text{CO}_2$  is passed through the liquid, which is kept cool, to saturation. A gelatinous mass results, which eventually crystallises. This is poured on to ice. The ether retains unaltered trimethyl-cyclo-hexanone, whilst by the addition of a dilute acid to the aqueous solution, trimethyl-cyclo-hexanone-carbonic acid is precipitated. To 100 parts of the sodium salt of this acid 4,000 parts of sodium amalgam (2 per cent.) are added, the solution being dilute and kept cold. A current of  $\text{CO}_2$  is passed through the liquid. When reaction is complete, dilute sulphuric acid is added, and trimethyl-oxy-cyclo-hexanone-carbonic acid is precipitated. The calcium salts of this acid and of formic acid are then distilled in equimolecular quantities in a current of hydrogen. The resulting cyclo-geraniolide-dene-aldehyde is rectified *in vacuo*, and 15 parts of the pure compound (which is a mixture of two isomers) are dissolved in 50 parts of acetone, and 0.75 part of sodium in 15 parts of absolute alcohol are added, the mixture being kept upon ice. The mixture is then neutralised. The  $\alpha$  and  $\beta$  ketones thus formed are separated by fractional distillation.

Maschmeyer (French Patent 354050 of 1905) has prepared methyl-cyclo-citrylidene-methoxy acetate by the condensation of citral with methyl chloracetate. The product has a strong violet odour.

Verley (English Patent 14613, 1897) has prepared a series of compounds having a violet odour depending on the reaction of an acid chloride on cymene in the presence of aluminium chloride. This results, for example, in the formation of propionyl-cymyl ketone. The ketone is brominated, and the bromo derivative is treated with sodium acetate, the acetic ether so obtained having an odour of orris root, or violet.

Hanriot communicated to the Eighth Congress of Applied Chemistry (New York, 1912) a characteristic colour reaction for the detection of ionone. The ionone is dissolved in concentrated hydrochloric acid. An intense golden yellow coloration is produced. If chloral hydrate be added and the liquid be heated, it turns a dirty violet colour. The liquid is allowed to cool and is shaken with ether. It is thus decolorised.

The ethereal solution, when evaporated in the cold on a watch glass, deposits a distinct violet colouring matter, soluble in water, instantaneously decolorised by ether. This last reaction is so delicate that it is sufficient to pour the vapours of ether on to the watch glass to produce the decolorisation of the violet substance.

Iso-ionone gives the same reaction. It is even probable that this reaction only occurs with ionone after its conversion into isoionone by the hydrochloric acid. As a matter of fact, it has not been possible to obtain the reaction in a neutral or alkaline medium.

Neither pseudoionone, nor oil of orris root, nor the natural oil of violets gives the reaction, which is sensitive with ionone in proportions of 1 in 2,000. It is thus possible to detect the presence of ionone in a large number of commercial perfumes.

The presence of the natural essential oils does not appear to interfere with the reaction.

**IRALDEINE.**—This name is that of one of the artificial violet perfumes. It is usually methylionone. (See "Ionone.")

**IRIS FLORENTINA.**—See "Orris Root."

**IRONE.**—See "Ionone."

**ISOAMYL ALCOHOL.**—This alcohol, of the formula  $(CH_3)_2CH(CH_2)_2OH$ , is found in the various eucalyptus oils, and also in geranium, lavender, and peppermint oils. It also occurs in the form of esters in the oils of *Eucalyptus globulus*, *Eucalyptus aggregata*, and in Roman camomile and cognac oils. It is an odorous liquid boiling at  $131^\circ$ , and yields a phenylurethane melting at  $51^\circ$  to  $52^\circ$ .

**ISOANETHOL.**—See "Estragol."

**ISOBORNEOL.**—Isoborneol is a stereoisomer of borneol,  $C_{10}H_{17}OH$  (*q.v.*). It closely resembles borneol in general characters. It results, together with borneol, on the reduction of the ketone, camphor, by means of sodium, or it may be prepared by causing the terpene camphene to take up water under the action of acetic and sulphuric acids. It may be prepared in the following manner. One hundred grams of camphene are heated, with 250 grams of glacial acetic acid and 10 grams of 50 per cent. sulphuric acid, to  $60^\circ$  for four hours, the mixture being continually shaken. When the reaction is complete, a large amount of water is added, when isobornyl acetate (formed by hydration of the terpene, accompanied by a molecular rearrangement, and acetylation of the so formed isoborneol) results. Excess of free acid is

washed away with water, and the separated ester is saponified in the usual manner by saponification under a reflux condenser. The greater part of the alcohol is distilled off, and the residual liquid is poured into a large volume of water. The isoborneol is precipitated, collected on a filter, washed with water, dried on a porous plate, and finally recrystallised from petroleum ether. The melting point of isoborneol is usually given as  $212^{\circ}$ , but according to Henderson and Heilbron (*Proc. Chem. Soc.*, 1913, 29, 381) it is  $217^{\circ}$ . Its specific rotation is  $\pm 34^{\circ}$ . On oxidation isoborneol yields camphor. It forms a phenyl-urethane melting at  $138^{\circ}$  to  $139^{\circ}$ . It can be easily differentiated from borneol by the fact that, on heating a solution of isoborneol in benzene for an hour with zinc chloride, camphene is obtained. Pure borneol under identical conditions remains practically unchanged.

**ISOBORNYL ACETATE.**—This ester,  $C_{10}H_{17}O_2C.CH_3$ , resembles bornyl acetate in its sharp fragrant odour. It is an oil of specific gravity 0.9905, and boils at  $107^{\circ}$  at 13 mm.

**ISOBORNYL FORMATE.**—This ester,  $C_{10}H_{17}O_2C.H$ , is a fragrant oil of specific gravity 1.017; it boils at  $100^{\circ}$  at 14 mm. pressure.

**ISOBUTYL ACETATE.**—This ester,  $(CH_3)_2CH.CH_2.COOCH_3$ , which has a fruity odour, has a specific gravity about 0.875, refractive index 1.3920, and boils between  $110^{\circ}$  and  $120^{\circ}$ . The commercial article is probably a mixture of isomers.

**ISOBUTYL ALCOHOL.**—This alcohol, of the formula  $(CH_3)_2CH.CH_2OH$ , is found in the distillation waters of *Eucalyptus amygdalina*. It boils at  $108^{\circ}$  to  $109^{\circ}$ , and has a specific gravity 0.8025. Its phenyl-urethane melts at  $80^{\circ}$ . It forms a number of highly aromatic esters which are useful in perfumery.

**ISOBUTYL BENZOATE.**—This ester,  $(CH_3)_2CH.CH_2.COO.C_6H_5$ , is an oil of very sweet odour, and is often sold as "Eglantine 100 per cent." It is used in the manufacture of sweet pea perfume. It is an oil of specific gravity 1.006, and refractive index 1.4942. It boils at  $237^{\circ}$  to  $238^{\circ}$ .

**ISOBUTYL BUTYRATE.**—This ester has a very fruity odour, and as met with in commerce is a mixture of isomers. It has a specific gravity about 0.865, and boils between  $152^{\circ}$  and  $158^{\circ}$ .

**ISOBUTYL FORMATE.**—This ester, which resembles the acetate, is an oil of specific gravity about 0.890, and boils at  $98^{\circ}$  to  $100^{\circ}$ .

**ISOBUTYL PHENYLACETATE.**—This ester, which sometimes enters into the composition of perfumes known as “Ideal” and “Eglantine,” is usually a mixture of isomers. It has a specific gravity about 0.990, refractive index 1.4860, and boils at 254°.

**ISOBUTYL PROPIONATE.**—This ester resembles the acetate, and has a fruity odour. It has a specific gravity about 0.896, and boils at 137° to 138°.

**ISOBUTYL SALICYLATE.**—This ester resembles amyl salicylate in odour, and is very useful in the preparation of artificial orchid perfumes and in such compositions as *trèfle*. It has the formula  $(\text{CH}_3)_2\text{CH}.\text{CH}_2\text{COO}.\text{C}_6\text{H}_4(\text{OH})$ . Its specific gravity is about 1.075; refractive index, 1.5100; and boiling point, 259° to 260°.

**ISOBUTYL VALERIANATE.**—This ester has a very fruity odour. The commercial article is a mixture of isomers having the following characters: specific gravity about 0.858 to 0.862; refractive index, 1.4057; and boils from 164° to 170°.

**ISOCARYOPHYLLENE.**—The sesquiterpene mixture isolated from oil of cloves on the extraction of the eugenol therefrom is, in reality, a mixture of two, if not three, sesquiterpenes. Similar mixtures exist in various other essential oils, such as pepper, cinnamon, and copaiba oils. (*Vide* “Caryophyllene.”) Deussen and Lewinsohn (*Annalen*, 356, 1; 359, 245) first showed that this was the fact. They separated the clove oil sesquiterpenes into two main fractions having the following characters:—

	1		2
Boiling point at 16 mm. .	132°–134°	..	128°–128.5°
Specific gravity at 20° .	0.903	..	0.910
Specific rotation . . .	– 4.67°	..	– 23.57°
Refractive index . . . .	1.4097	..	1.4990

Of these, No. 1 was probably optically inactive, but contaminated with a small amount of optically active sesquiterpene. To this Deussen gave the name  $\alpha$ -caryophyllene, and to the optically active body the name  $\beta$ -caryophyllene. A third isomer was separated, boiling at 124° to 125° at 14 mm., and having a specific rotation – 22.22°. This body appears to be identical with what was then known as isocaryophyllene, and to it Deussen gave the name  $\gamma$ -caryophyllene. Semmler and Mayer (*Berichte*, 44, 3657) agree generally with Deussen, but have much complicated the whole matter by introducing a fresh and empirical



nomenclature. They agree with Deussen that crude caryophyllene consists of three distinct individuals. They maintain that Deussen's  $\alpha$ -caryophyllene is identical with Chapman's humulene, isolated from oil of hops (without, in the writer's opinion, sufficient experimental evidence). The two other isomers they suggest naming *terp*-caryophyllene, on account of some relationship they think exists with terpinolene, and *lim*-caryophyllene, on account of a similar relationship with limonene. (For further details of this very complicated subject, reference may be made to E. J. Parry, "The Chemistry of Essential Oils, etc.," 4th ed., vol. ii., pp. 84-88.) From the perfumer's point of view, caryophyllene may be regarded as the main constituent of the light oil of cloves obtained on extraction of the eugenol, and which is very useful in cheap soap perfumery where a clove or carnation perfume is desired.

**ISOESTRAGOL.**—See "Anethol."

**ISOEUGENOL.**—Isoeugenol,  $C_{10}H_{12}O_2$ , is a phenol which is found to a very small extent in nature, but which is of extreme importance to the perfumer. It exists in minute quantities in the essential oils of ylang-ylang, champaca, and nutmeg. It is, however, produced on an enormous scale by the isomerisation of eugenol (see "Eugenol" and "Carnation") as an intermediate step in the manufacture of that most important substance, vanillin, from oil of cloves. A considerable quantity, however, is sold as such to perfumers for the manufacture of artificial carnation and similar perfumes. Its odour, being somewhat "heavy," adapts it to the preparation, when suitably blended, of perfumes of the so-called Oriental type.

Isoeugenol is a pale yellow to colourless oil of powerful clove-carnation odour, having the following characters:—

Boiling point at 760 mm.	. . .	263°
Boiling point at 4 mm.	. . .	112°
Specific gravity	. . .	1.089
Refractive index	. . .	1.5736
Optical rotation	. . .	0°

When cooled to a low temperature, isoeugenol solidifies, and melts at 34°, but as commercial specimens invariably contain traces of impurities, it is always liquid, in a state of superfusion. The industrial preparation of isoeugenol is a matter of considerable magnitude, and numerous patents have been taken out for its manufacture. In the early days of vanillin manufacture the

principal difficulty was the fact that in the isomerisation process isoeugenol showed a great tendency to give rise to polymerisation products and tarry matters. The principal methods which have been used are the following. In 1890 Haarmann and Reimer (German patent No. 57808) recommended heating the eugenol with a saturated solution of caustic potash in amyl alcohol. The temperature is maintained at  $140^{\circ}$  for about twenty-four hours. The isoeugenol is thrown out of solution by the addition of a dilute acid, and rectified. De Laire (French patent of 1890, No. 209149) recommended as an alternative, heating in an autoclave to a temperature of  $100^{\circ}$  to  $160^{\circ}$  of a concentrated solution of potassium-eugenol. Kolbe (French patent of 1891, No. 213892) preferred an ethyl alcohol solution of caustic potash for isomerisation. Einhorn (German patent No. 76982 of April 5th, 1892) recommended the use of anhydrous caustic potash with eugenol at a temperature of  $230^{\circ}$ . The yield is proportional to the rapidity with which the mass is heated to the maximum temperature. Schleich (French patent No. 239197 of June, 1924) prefers to heat the eugenol with a glycerine solution of caustic potash for six hours at about  $230^{\circ}$ .

Einhorn's process is one which gives a very satisfactory yield, and is very commonly employed. The oxidation of isoeugenol will be dealt with under "Vanillin." Isoeugenol forms numerous crystalline compounds which serve for its identification. Monobromisoeugenoldibromide melts at  $138^{\circ}$  to  $139^{\circ}$ . If eugenol be acetylated for five hours, acetyl-isoeugenol results, which, if dissolved in benzene and precipitated by petroleum ether, melts at  $79^{\circ}$  to  $80^{\circ}$ . Benzoyl-isoeugenol is prepared by the interaction of isoeugenol, benzoyl chloride, and caustic soda. It melts at  $104^{\circ}$  to  $105^{\circ}$ . Isoeugenol also forms a diphenyl-urethane melting at  $112^{\circ}$  to  $113^{\circ}$ .

Isoeugenol usually gives the best results when used in conjunction with a little eugenol, the former having a more typical carnation odour, and the latter a more typical clove odour. This mixture is quite indispensable in the preparation of perfumes of the "œillet" type.

**ISOGERANIOL.**—This body is an alcohol having a sweet rose odour, resulting from enolising citral with acetic anhydride. An internal rearrangement of the position of a double bond thus takes place, and the acetic ester of *enol*-citral results. By the reduction of this body by means of sodium amalgam, and methyl alcohol slightly acidified with acetic acid, isogeraniol results.

Isogeraniol boils at 103° at 9 mm. pressure, and has a specific gravity 0.879 at 20°, and refractive index 1.4730. It forms a diphenylurethane, melting at 73°, and an oily tetrabromide.

**ISOPROPYL ALCOHOL.**—*Vide* "Alcohol, Isopropyl."

**ISOPROPYL-*o*-CRESOL.**—This is a synonym of carvacrol (*q.v.*).

**ISOSAFROL.**—This body is the methylene ether of propenyl-dioxy-benzene, so it is related to safrol, which is the methylene ether of allyl-dioxy-benzene, in the same manner as isoeugenol is to eugenol. Isosafrol,  $C_{10}H_{10}O_2$ , is a highly odorous liquid, having a specific gravity 1.1255; boiling point, 254°; refractive index, 1.5780. It is optically inactive. Both safrol and isosafrol yield heliotropin (*q.v.*) on oxidation, but as a much higher yield is obtained from isosafrol, the conversion of safrol into isosafrol is always a preliminary step in the manufacture of heliotropin. Safrol constitutes the principal part of oil of sassafras, but as it exists in considerable quantity in camphor oil, the commercial supply is derived entirely from the latter oil. Safrol is heated for twenty-four hours with 2.5 parts of caustic potash and 5 parts of 90 per cent. alcohol. At the end of this period an excess of water is added, and after recovering the alcohol by distillation, the reaction mass is extracted with ether. The isosafrol so obtained is dried over calcium chloride and rectified. Variations in the methods of isomerisation are similar to those for eugenol. (*Vide* "Isoeugenol.") Isosafrol is actually a mixture of two stereoisomers.

Höring and Baum (*Berichte*, 42, 3076) have succeeded in isolating these two isomerides. They have worked with the isosafrol of commerce, which is a mixture of  $\alpha$ - and  $\beta$ -isosafrol with safrol.  $\beta$ -Isosafrol is contained in the fractions of high boiling point, from which it may be extracted in the pure state, owing to its property of forming a stable picrate, melting at 74°.

$\beta$ -Isosafrol may be separated from the safrol with which it is mixed, by the formation of a mercurial compound, which is produced by the action of mercuric acetate and calcium chloride.

The characters of the two isomerides are as follows:—

*$\alpha$ -Isosafrol*

Boiling point (743 mm.)	.	.	241°–242.5°
Specific gravity at 18.5°	.	.	1.1073
Refractive index at 18°	.	.	1.5678

*β-Isosafrol*

Boiling point (743 mm.)	. . .	251°–251.3°
Specific gravity at 17.5°	. . .	1.1227
Refractive index at 18°	. . .	1.5786

ISOSANTALENE.—See “Santalene.”

ISOVALERIANIC ALDEHYDE.—This aldehyde, of the formula  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CHO}$ , has been isolated from American peppermint oil. It is a volatile liquid, boiling at 92.5°, and having a specific gravity 0.804. It forms a thiosemicarbazone melting at 53°.

IVA OIL.—See “*Achillea Moschata*.”

JACINTHE.—= Hyacinth (*q.v.*).

JARACANDA.—This is a native name for bois de rose (*q.v.*).

JASMAL.—See “Phenyl-glycol-methylene-acetal.”

JASMINE.—The perfume of this beautiful flower has always been highly esteemed. The flowers are cultivated to a large extent in the south of France, the crop being gathered almost continuously from July to October. The jasmine is a member of the natural order *Oleaceæ*, and is probably a native of India. Donald McDonald (“Fragrant Flowers and Leaves,” 1895, 59) gives the following account of the introduction of the jasmine plant into Italy, which is probably only legendary. One of the early Dukes of Tuscany was the first owner in Italy of a plant, and as he wished to retain it as a novelty, he forbade his gardener to give away any cuttings of it. The gardener, however, disobeyed his orders and gave his mistress a bunch of the flowers as a birthday offering. She was so pleased with their perfume that she struck some of the branches, and by careful cultivation produced large quantities of flowers, which she sold to such advantage that she amassed a fortune and married the gardener.

There are about 100 species of jasmine recognised, mostly natives of India, Arabia, or China. The species principally cultivated in the south of France for the perfume is *Jasminum grandiflorum*, the so-called Spanish or Catalanian jasmine; it is usually grafted on to cuttings of *Jasminum officinale*. The cuttings are allowed to become well developed, and as soon as they are strong enough the yellow plants are grafted on, and the plants are left to their second year. The flowers are picked as soon as possible after they open, which is usually in the evening in July to the middle of

August, and in the early morning after that time. The essential oil of jasmine is not prepared on a commercial scale, the natural jasmine perfume being marketed as an enfleurage or similar product. A very large amount of the jasmine perfume of commerce, however, is partially or entirely artificial.

The jasmine plant and its perfume has been of considerable value in tracing the development of the perfume in the plant tissues. Hesse, for example, has shown that when the flower is extracted by means of a volatile solvent the essential oil does not contain either methyl anthranilate or indol, whereas when extracted by the enfleurage process, so that the life processes in the flower can continue for some time, there is a prolonged production of essential oil due to the decomposition of a glucoside, and not only is a larger yield of essential oil obtained, but both methyl anthranilate and indol appear as new constituents of the oil. (See also Charabot and Gatin, "La parfum chez la plante," Paris, 1908). Nivière (*Bull. Soc. Chim.*, 1920, 27, 862) has shown that if the jasmine flowers are submitted to a preliminary hydrolysis by acids or enzymes before extraction with a volatile solvent, a higher yield of oil is obtained. Mesnard has also used the jasmine flower for his investigations ("Recherches sur le mode de production du parfum dans les fleurs": E. Mesnard, présentée à l'Académie par Duchartre, *Comptes Rendus*, 1892, cxv., 282). He states that in the jasmine flower, the essential oil is situated in the row of epidermal cells on the upper side of the sepals and petals. Some exists also in the corresponding layer on the under surface, where the sepals are coloured by a violet pigment. If the evolution of the cell contents in flowers at different stages of development be followed, at first nothing but chlorophyll is found in the tissues. Tannic acid next appears, or glucosides which yield tannic acid on hydrolysis. These glucosides also yield the pigments of the lower surface of the sepals. Hydrochloric acid gas serves as a reagent to distinguish between the intermediate compounds between the chlorophyll, on the one hand, and the tannic acid, pigments, and essential oil on the other. Apparently in the lower surface, which in the bud state was exposed to the light and air, the intermediate tannoid bodies are slowly oxidised and give rise to tannic acid, whilst on the upper surface, being hidden inside the bud, these agencies are inoperative, and the same compounds are decomposed in a different manner with the production of essential oil.

Jasmine oil obtained from the pomade varies considerably,

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according to the exact method of production. The specific gravity may be as low as 0.920 or as high as 1.015. The optical rotation lies between  $-1^{\circ}$  and  $+5^{\circ}$ , the ester value between 40 and 72 per cent., calculated as benzyl acetate.

Verley (*Comptes Rendus*, 1899, 128, 314; *Bull. Soc. Chim.*, 1899, iii., 21, 226) investigated the oil extracted from the pomade by means of acetone, and stated that the oil consisted of approximately 10 per cent. of linalol and 90 per cent. of phenyl-glycol-methylene-acetal, which he termed jasmal. The result of this work was a French patent for the production of jasmal synthetically. Hesse and Müller (*Berichte*, 1899, 32, 565, 765) showed later that this body did not exist in jasmine oil. They found then (and later, *Berichte*, 1901, 34, 291) that the oil had the following composition:—

	Per cent.
Benzyl acetate . . . . .	65
Linalyl acetate . . . . .	7.5
Linalol . . . . .	15.5
Benzoyl alcohol . . . . .	6
Indol . . . . .	2.5
Jasmone . . . . .	3
Methyl anthranilate . . . . .	0.5

Traces of *para*-cresol and geraniol are also probably present.

Hesse and Müller (*loc. cit.*) give the following characters for ten samples of oil which they examined:—

	Specific gravity.	Rotation.	Esters as benzyl acetate.
			Per cent.
1 .	1.015	$+2^{\circ}30'$	73
2 .	1.018	$+2^{\circ}30'$	70
3 .	1.011	$+2^{\circ}30'$	72.9
4 .	1.009	$+3^{\circ}30'$	70.4
5 .	1.006	$+3^{\circ}15'$	69.1
6 .	1.007	$+3^{\circ}10'$	70.7
7 .	1.014	$+3^{\circ}20'$	71
8 .	1.012	$+3^{\circ}10'$	72
9 .	1.000	$+3^{\circ}30'$	73
10 .	1.015	$+3^{\circ}20'$	71.4

The body jasmone is a ketone of the formula  $C_{11}H_{16}O$ , of specific gravity 0.945, boiling at  $258^{\circ}$  at a pressure of 775 mm. It yields an oxime melting at  $45^{\circ}$ , and a semicarbazone melting at  $201^{\circ}$  to  $204^{\circ}$ .

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The commercial product sold as jasmine oil (apart from the absolutes and concretes) is artificial, and is based invariably on benzyl acetate, which has a marked odour of the flower. Sometimes this ester is modified with a little benzyl formate and a little linalyl acetate. Free alcohols, linalol, benzyl alcohol, and traces of geraniol are usually present, and traces of benzyl propionate, cresylphenylacetate, and phenyl-ethyl alcohol are often used. A little methyl anthranilate and indol are generally employed, unless an absolutely colourless product is desired, when the indol must be omitted. Traces of decylic aldehyde, phenylacetic acid, and a little natural jasmine will improve the artificial product considerably.

*Jasminum odoratissimum* is a native of Madeira which is cultivated in Formosa for the purpose of perfuming tea. The yellow flowers, which retain their perfume when dried, are known as Shuei flowers.

R. Tsuchihashi and S. Tasaki (*Jour. Soc. Chem. Ind.*, 1919, 38, 117) have treated these flowers by means of petroleum ether and obtained a solid essential oil with a yield of 0.277 per cent. This solid, exhausted with alcohol, yielded 0.116 per cent. of essential oil and 0.161 per cent. of wax.

The essential oil thus obtained is a reddish-brown liquid, which has the following constants :—

Specific gravity . . . . .	0.9309
Optical rotation . . . . .	+ 5.64°
Refractive index . . . . .	1.4845
Acid value . . . . .	5.85
Saponification value . . . . .	92.25
Saponification value after acetylation . . . . .	186.20

It distils between 60° and 200°, and its composition is as follows : 6 per cent. linalol, 6 per cent. linalyl acetate, 1.6 per cent. benzyl alcohol, 6 per cent. benzyl acetate, 10 per cent. methyl anthranilate and indol.

Fifty-seven per cent. of the oil is composed of a diterpene and a sesquiterpene alcohol, which are found in the fractions with high boiling points. The authors found no jasmone in this essential oil.

Treatment of the flowers of *Jasminum odoratissimum* by enfleurage in the cold gave no result.

*Jasminum sambac* is a native of Arabia which grows wild in profusion in India. Its flowers are delightfully fragrant. The so-called Tuscan jasmine is *Jasminum trifoliatum*, known in India

as *kadda-mulla*. Numerous other species bear very fragrant flowers, but their perfume is not extracted.

**JONQUIL.**—The jonquil is *Narcissus Jonquilla* (see “Narcissus”), one of the highly-scented flowers of the natural order *Amaryllidaceæ*. The natural perfume is extracted by the enfleurage process, and can also be produced as a concrete, but the essential oil is not manufactured. Artificial jonquil is very similar to artificial narcissus and hyacinth (*q.v.*). As a rule, however, phenyl-ethyl phenylacetate is used in jonquil with a trace of patchouli oil.

**JUNIPER OIL.**—Juniper oil is the distillate of the berries of *Juniperus communis*, one of the *Coniferæ*, growing commonly in many parts of Europe. The oil is only used to a very limited extent in actual perfumery, but is used to a considerable extent in the allied industry of flavouring liqueurs and cordials. Juniper is the basis of all gin flavours. The common juniper is a native of Greece, forming a small shrub in most parts of Europe, but growing to 30 or 40 feet high in Scandinavia. *Schimmel & Co.* give the following as the average yield of oil from juniper berries of various origins :—

	Per cent.		Per cent.
Bavarian.	1.2	East Prussian	0.6
Thuringian	0.7	Swedish	0.5
Italian	1-1.5	Polish	0.9
Hungarian	0.8-1		

Much of the juniper oil of commerce is deprived of its principal flavouring ingredients, so that it is really only a light oil of juniper containing little other than terpenes. Juniper oil contains pinene, camphene, cadinene, and a small amount of oxygenated constituents. Amongst these latter is terpinenol and an alcohol not yet identified, but having a specific gravity 0.9476; optical rotation, — 4° 30'; refractive index, 1.4835; and boiling point, 218° to 226°. It is in all probability a sesquiterpene alcohol. Traces of esters are also present.

Juniper oil is an oil which rapidly oxidises on keeping, with the formation of insoluble constituents. An oil kept under fair average conditions will have the following characters :—

Specific gravity	0.865-0.890
Optical rotation	— 3° to — 20°
Refractive index	1.4750-1.4880
Ester value	2-8
Ester value after acetylation	15-25



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Occasionally a sample is found to be dextrorotatory to the extent of  $+1^{\circ}$  or  $+2^{\circ}$ . Samples with specific gravities above 0.890 are usually so old as to be of little flavouring value.

The essential oil distilled from the berries of *Juniperus phœnicea*, which is found in Sardinia and Cyprus, is highly aromatic. It has been examined by Puxeddu and Vodret (*Gaz. Chim. Ital.*, 1920, 50, ii., 245-257), who state that, when distilled with water, the macerated berries of the plant yield 2.5 per cent. of essential oil, four-fifths of this amount distilling over during the first hour, while the remainder requires about five hours; the preliminary maceration with water should last at least two days. The oil is neutral, colourless, and transparent, but turns slightly yellow under the influence of light. Its taste resembles that of camphor, and it has a marked aromatic odour, while when rubbed between the hands it emits the odour of turpentine. It burns with emission of dense smoke and resinous odour. It has a specific gravity = 0.8658 at  $15^{\circ}\text{C}$ ., and specific rotation  $+16.84^{\circ}$ .

**KÆMPFERIA ETHELÆ.**—The essential oil distilled from the tubers of *Kæmpferia Ethelæ*, a plant belonging to the natural order *Zingiberaceæ*, has been examined by Goulding and Roberts (*Jour. Chem. Soc.*, 1915, 314). The yield was about 2 per cent. on the dry material, of an oil having an odour somewhat resembling that of neroli oil, with a suggestion of crushed ivy leaves. The oil has the following characters:—

Specific gravity . . . . .	0.923-0.944
Optical rotation . . . . .	$+19^{\circ}47'$ to $+30^{\circ}4'$
Acid value . . . . .	1.0-2.3
Ester value . . . . .	5-11.5
Ester value after acetylation . . . . .	33.6-47.6

The dried bulbs, or tubers, which occur in north-eastern Transvaal, are there known as *Sherungulu*.

The composition of the oil is given as follows:—

	Per cent.
Terpenes . . . . .	21.8
Cineol . . . . .	17.2
Kæmpferia ketone . . . . .	13.0
Alcohols (including linalol) . . . . .	11.2
Esters (chiefly methyl anthranilate) . . . . .	1.3
Phenols . . . . .	0.5
Acids (free) . . . . .	0.1
Residue (chiefly sesquiterpene) . . . . .	34.9

The ketone present in this oil is a crystalline body, of the

formula  $C_{24}H_{28}O_4$ , melting at  $102^\circ$ , and having a specific rotation  $+198^\circ$  in chloroformic solution. In dilute alcoholic solution this body has a distinct odour of crushed ivy leaves. It yields a hydroxylamine oxime melting at  $184^\circ$ , and an oxime melting at  $166^\circ$ .

**KÆMPFERIA GALANGA.**—The roots of this species of *Kæmpferia* yield a heavy essential oil of specific gravity about 1.025; optical rotation,  $-16^\circ$ ; and refractive index, 1.5428. It contains ethyl cinnamate and ethyl-*para*-methoxy-cinnamate.

**KAOLIN.**—This substance is used to a small extent in the preparation of toilet powders, and also to some extent as a filtering powder. It is a white or greyish-white porcelain clay resulting from the decomposition of felspathic rocks, and consists mainly of one or more silicates of aluminium, with small quantities of other inorganic substances.

**KAPUR-KACHRI.**—The dried root of *Hedychium spicatum*, an Oriental plant belonging to the natural order *Zingiberaceæ*, is much valued in the East, especially by the Arabs and Persians, as a perfume, and is used by the Hindoos as incense for ceremonial purposes. The name (see Sawyer, "Odorographia," series ii., p. 72) is derived from the Greek, and means "sweet show," in allusion to the elegance, fragrance, and whiteness of the flowers of the first named species of the genus, *Hedychium coronarium*. *H. spicatum* is a native of Sepal and Silhet, and is fairly common in the Punjab Himalayas. According to Dymock, the dried root forms a considerable article of commerce in India and China, and is also exported to Europe. Two varieties are well recognised, the Indian and the Chinese. The Indian kapur-kachri was formerly believed to be identical with the so-called "lesser galangal root," but this is now known to be incorrect. J. T. Thresh (*Pharm. Jour.*, 3, xv., 361) describes the odour as intermediate between storax and rhubarb root, whilst Dymock prefers to say that it recalls that of orris root and camphor. Thresh (*loc. cit.*) states that the amount of actual odoriferous material is very small, but that it is very powerful. A minute quantity, exposed to the air, recalls the odour of hyacinths. He extracted the roots with petroleum ether. On allowing the solvent to evaporate slowly, a crop of large, colourless, tabular crystals was obtained, which when recrystallised, melted at  $49^\circ$ . This body appears to be ethyl-methyl-paracoumarate, but it is not the odour bearer of the root, which has not been isolated and identified. Numerous other species of

hedychium are cultivated, but have not been examined to any extent, from their perfume point of view. The essential oil of *Hedychium coronarium* has been found to have a specific gravity 0·869, and an optical rotation —  $0^{\circ} 28'$  (*Schimmel & Co., Bericht*, April, 1894, 58). A Brazilian plant of this species was found by Peckolt (*Pharm. Rund. New York*, 1893, 11, 287) to have similar characters.

**KESSO OIL.**—Kesso oil is the name given to Japanese valerian oil, distilled from the roots of *Valeriana officinalis*, var. *angustifolia*. The yield is high, sometimes reaching as much as 8 per cent. This (and other valerian oil) is used to a small extent in certain soap perfumes. The Japanese oil has the following characters :—

Specific gravity	.	.	.	0·965–1·000
Optical rotation	.	.	.	— $20^{\circ}$ to — $35^{\circ}$
Refractive index	.	.	.	1·4775–1·4875
Acid value	.	.	.	1–20
Ester value	.	.	.	90–135

It has been examined by Bertram and Gildemeister (*Arch. der Pharm.*, 1890, 228, 483). These chemists have identified the following bodies in the oil: pinene, camphene, dipentene, terpineol; borneol, bornyl acetate, bornyl isovalerianate, a sesquiterpene, a blue oil not yet identified, and an ester which has been termed kessyl acetate,  $C_{14}H_{23}O.COOCH_3$ . This body is the acetic ester of kessyl alcohol,  $C_{14}H_{23}O_2$ , a crystalline body, melting at  $85^{\circ}$ , and boiling at  $300^{\circ}$  to  $302^{\circ}$ . The acetate boils at  $179^{\circ}$  at 16 mm. pressure, and has an optical rotation —  $70^{\circ} 6'$ .

**KOBUSHI OIL.**—The fresh leaves and branches of the Kobushi tree (*Magnolia Kobus*) yield about 0·45 per cent. of a highly odorous essential oil, of specific gravity about 0·964; optical rotation, —  $1^{\circ} 6'$ ; and ester number, 8·9. It has an odour of sassafras. The oil contains eugenol, cineol, citral, methyl chavicol, and other bodies. The tree flourishes in central Japan. (See “*Magnolia*.”)

**KUNZEA CORIFOLIA.**—This plant is a very common so-called “tea tree” growing in the Port Jackson district in Australia, and although it has become less plentiful than it used to be, owing to the rapid spread of population, many luxuriant patches are still to be found in the neighbourhood of Sydney. The leaves and terminal branchlets yield a very

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fragrant essential oil, which has been investigated by F. R. Morrison (*Jour. and Proc. Roy. Soc. of N.S.W.*, 1923, lvi., 201).

A total weight of 387 kg. of leaves and terminal branchlets, cut as for commercial distillation, was submitted to distillation with steam and gave an average percentage yield of oil of about 0.35 per cent., varying from 0.26 to 0.52 per cent. The highest percentage yield was obtained from material collected at Waverley, on the sea coast, the other localities being some distance therefrom.

The 387 kg. of leaves and terminal branchlets gave on steam distillation crude oils possessing physical and chemical characteristics as follows :—

Date.	Locality from which material was obtained.	Weight of leaves. Kilos.	Percent- age yield.	Specific gravity at 15/15°.	Optical rotation.	Refractive index at 20°.
27/1/1921	Gore Hill	154	0.26	0.9103	+ 18.6°	1.4902
10/10/1921	Waverley	174	0.52	0.9112	+ 12.0°	1.4893
20/7/1922	Longueville	22	0.32	0.9087	+ 24.0°	1.4837
5/10/1922	Hornsby	36	0.28	0.8917	+ 25.6°	1.4801

Ester no., hot 1½ hours.	Ester no. after acetyla- tion, hot 1½ hours.	Ester no. after acetyla- tion, cold 2 hours.	Solubility of oil in 80 per cent. alcohol (by weight).	Colour of oil.
13.0	49.22	—	Insoluble in 10 vols.	Brown
9.94	57.58	31.78	Insoluble in 10 vols.	Dark brown
15.48	66.66	34.89	Soluble in 10 vols.	Light green
13.56	39.19	15.57	Insoluble in 10 vols.	Light brown

The crude oils, on distillation, gave the following results: January 27th, 1921, 32 per cent. distilled between 40° and 50° at 10 mm.; 5 per cent. between 50° and 100°; and 54 per cent. between 100° and 140°. October 10th, 1921, 36 per cent. distilled below 185° at 762 mm.

*Determination of the Terpene.*—The lower boiling fraction in each case was submitted to repeated distillation, over 80 per cent. distilling below 160° at 766 mm. It was found to consist principally of d- $\alpha$ -pinene, which gave the following constants: January 27th, 1921, boiling point, 155° to 157°; specific gravity  $\frac{15^\circ}{15}$ , 0.8613; optical rotation, + 40.6°; and refractive index 20°, 1.4655. October 10th, 1921, boiling point, 155° to 157°; specific

gravity  $\frac{15^\circ}{15}$ , 0.8623; optical rotation,  $+ 39.9^\circ$ ; refractive index  $20^\circ$ , 1.4651.

Confirmatory evidence of its identity was established by preparation of the following derivatives:—

On account of the high optical rotation the terpene failed to give a nitrosochloride; on mixing, however, with an equal volume of *lævo*-pinene ( $\alpha$ )<sub>D</sub>  $- 50.18^\circ$ , which by itself failed to give a nitrosochloride, an excellent yield of the derivative was obtained which, when purified, melted at  $104^\circ$ .

The hydrochloride, prepared by saturating 5 c.c. of the terpene at  $- 20^\circ$  with dry hydrochloric acid gas, resembled camphor, and after recrystallisation from alcohol, melted at  $127^\circ$ .

*Oxidation of the Terpene.*—58 c.c. were shaken with 120 grams of potassium permanganate, 1,000 c.c. of water, and 500 grams of ice until completion of reaction. The liquid was passed through a suction filter, whereby the manganese sludge was removed, and the clear liquid then evaporated to small bulk. It was then steam distilled in order to remove unchanged terpene, and again concentrated by evaporation. Dilute sulphuric acid was then added, the liberated pinonic acid extracted with chloroform, which latter solvent was distilled off, and the crude acid distilled at 5 mm. pressure, when the greater portion came over at  $180^\circ$  to  $181^\circ$  C. After standing for some considerable period crystals separated, and these were removed by filtration. On recrystallisation from petroleum ether the crystals melted at  $68^\circ$ ; 0.1704 gram of the pure acid dissolved in 10 c.c. chloroform rotated the plane of polarised light  $+ 1.7^\circ$ . Specific rotation, ( $\alpha$ )<sub>D</sub>  $+ 100^\circ$ . The semicarbazone was prepared, and after recrystallisation from alcohol melted at  $207^\circ$  C. The terpene is therefore d- $\alpha$ -pinene.

*Determination of the Sesquiterpene.*—That portion of the Gore Hill sample of oil distilling between  $100^\circ$  to  $140^\circ$  (principally  $120^\circ$  to  $140^\circ$ ) and the higher boiling portion of the Waverley sample were allowed to stand over metallic sodium for a week, and repeatedly fractionated over that metal until a main fraction was obtained, which possessed the following characters:—

Gore Hill: boiling point,  $129^\circ$  to  $132^\circ$  at 10 mm.; specific gravity  $\frac{15^\circ}{15}$ , 0.9218; optical rotation,  $+ 6^\circ$ ; refractive index at  $20^\circ$ , 1.5056.

Waverley: boiling point,  $129^\circ$  to  $132^\circ$  at 10 mm.; specific

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gravity  $\frac{15^\circ}{15}$ , 0.9239; optical rotation,  $-2.1^\circ$ ; refractive index at  $20^\circ$ , 1.5046.

*Preparation of the Hydrochloride.*—Five c.c. of the sesquiterpene were dissolved in 10 c.c. of perfectly dry ether, the vessel placed in a mixture of ice and salt at  $-20^\circ$ , and the solution saturated with dry hydrochloric acid gas. It was allowed to stand overnight, when crystals separated. On recrystallisation from alcohol they formed beautiful needles, melting at  $115^\circ$  to  $116^\circ$ ; 0.1162 gram dissolved in 10 c.c. chloroform gave optical rotation  $-0.65^\circ$  ( $a$ )<sub>D</sub>  $-39.11^\circ$ .

The sesquiterpene which gives a corresponding derivative with hydrochloric acid gas to that obtained as above, is cadinene, which, according to Parry ("Chemistry of Essential Oils, 2nd ed., p. 73) possesses the following characters: boiling point,  $272^\circ$  to  $275^\circ$  at atmospheric pressure; specific gravity, 0.9215; refractive index, 1.5065; optical rotation,  $-105^\circ$ ; melting point of dihydrochloride,  $117^\circ$  to  $118^\circ$ ; and specific rotation in chloroform solution,  $-37^\circ$ .

Attempts to prepare the nitrosochloride and nitrosate were unsuccessful, but the evidence so far obtained indicates that the sesquiterpene occurring in the oil is probably identical with cadinene.

*Alcohols.*—The saponification values after acetylation of the crude oils indicate the presence of fair quantities of alcoholic bodies in the oils. The only portion, however, in which these bodies appeared to be concentrated was a small fraction boiling between  $160^\circ$  to  $185^\circ$ . This fraction was shaken with 50 per cent. resorcin solution, and on steam distillation 5 c.c. of a light blue oil were obtained which had the characteristic fragrant odour possessed to a lesser degree by the crude oil. The constituent thus obtained had the following characters: specific gravity  $\frac{15^\circ}{15}$ , 0.9029; optical rotation,  $+6.2^\circ$ ; refractive index at  $20^\circ$ , 1.4685.

**KUROMOJI OIL.**—The leaves and young twigs of the Japanese plant *Lindera sericea*, one of the *Lauraceæ*, yield an essential oil having a very fragrant odour recalling that of the myrtle. The native name for the shrub is *Kuro-moji*, an allusion to the very dark colour of its bark.

The oil obtainable in commerce is that distilled from the leaves and young twigs, and is a dark yellowish oil of powerful balsamic

odour. It has a specific gravity 0.890 to 0.915, and is usually slightly laevorotatory. It has been investigated by Kwasnik (*Arch. du Pharm.*, 1892, 230, 265) and found to contain *d*-limonene, dipentene, terpineol, and carvone. An oil distilled by *Schimmel & Co.* from similar material was found to contain 9.5 per cent. of esters calculated as geranyl acetate. Linalol was also detected in the oil. Shinohara has recently investigated this oil, and states that it contains 11.4 per cent. of esters, 20 per cent. of free alcohols, 7.7 per cent. of cineol, 51 per cent. of terpenes, 9.2 per cent. of aldehydes and ketones, and traces of phenols and free acids. The free alcohols consist of linalol and geraniol. The oil distilled from the remainder of the shrub was also found by *Schimmel & Co.* (*Bericht*, April, 1904, 98; 1907, 67) to contain cineol, linalol, geraniol, and geranyl esters.

**LABDANUM.**—This resinous material is an exceedingly valuable raw material for the perfumer. It has for many years been used in the Near East as a fumigating perfume, and has in recent years become very much esteemed as a perfume material in western Europe and America. It is an oleoresinous substance obtained from species of *Cistus*. In olden days labdanum was very highly appreciated as a medicament. Its resinous, balsamic, and stimulating properties caused it to be used in ailments of the stomach and liver, and also as a remedy against loss of hair. It is to-day used, *inter alia*, as an ingredient in some types of fumigating pastilles—*pastilles du Sérail*. The principal species from which the oleo-resin is obtained are *Cistus ladaniferus* and *Cistus creticus*, which are found dispersed all over the island of Cyprus, and *Cistus monspeliensis*, which is found in Greece. *Cistus ladaniferus* is also found in Portugal and Spain. Several hybrids are also known which yield a certain amount of the oleoresin. Formerly the oleoresin was collected by the shepherds combing it from the fleeces of sheep that had been browsing amongst the *cistus* bushes and so loaded their wool with the sticky exudation. In Crete a special instrument is used for collecting the resin which is called a *ladanisterion*, a sort of double rake with leathern thongs. It appears that this method of collecting labdanum does not differ materially from that given by Dioscorides in the first century (Tournefort, "Voyage to the Levant," i., pp. 56-60, London, 1718). To-day the shep are not troubled much, and the collection is almost entirely by means of these leather rakes, which are used to rub against the younger parts of the plant and

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then rubbed in sand to facilitate the removal of the resin. Sometimes, also, the branches are boiled in water and the resin skimmed from the surface. The plants yield the oleo-resin most freely from May to July, and round about noonday is the best time for collection.

Holmes (*P. & E. O. R.*, 1911, 155) has shown that Spanish labdanum is obtained from *Cistus ladaniferus* var. *macellatus*.

The botanical characters of the principal *Cistus* species have been studied recently by A. Camus (*Bulletin, Roure-Bertrand Fils*, October, 1920, 3). Labdanum occurs in dark brown to blackish viscid masses with a heavy languorous odour recalling the heavy type of Oriental perfume. It softens on handling, and exhibits a greyish surface when broken, which quickly becomes black on exposure to the air. It is, of course, insoluble in water, but is almost completely soluble in alcohol. It is sometimes adulterated with cheaper resins. Very few authentic samples of labdanum have been examined, so that the following values must be accepted with reserve. Dieterich ("Analysis of Resins") gives the following figures :—

	Acid value.	Ester value.	Saponification value.
French commercial	90.37	116.1	206.47
	91.98	120.26	212.24
	98.05	102.06	200.11
	98.36	109.88	208.24
German commercial	54.08	167.87	221.95
	54.69	161.95	216.64
	54.01	166.88	220.89
	51.85	168.39	220.24
Cretan commercial	113.81	87.88	201.69
	114.80	87.98	202.78

E. J. Emanuel has examined this substance, and gives the following as its characters :—

	Per cent.
Resin extracted by ether	48
Resin by alcohol after ether	17
Essential oil	2
Ladaniol (guaïol ?)	0.8
Gum	3.5
Mineral matter	12

The most recent and authentic contributions to the know-



ledge of labdanum are those of Gérardin (*Bull. des Sciences pharmacologiques*, 1919, 6, 289), and Gérardin and Gattefossé (*La Parfumerie Moderne*, 1920, 6, 111).

According to Gérardin, labdanum was formerly placed on the market in the following forms :—

“ In cakes, sticky and blackish lumps.

“ In small balls, the best coming from Cyprus (Schroder, seventeenth century).

“ In twists or in cords. The material, drawn out into rods, was twisted into the shape of a ram's horn, or like tapers (cellar tapers), Spanish liquorice, or chewing tobacco.

“ Rolled warm, twisted and ornamented with designs (?). This peculiarity is met with in Morelot's 'Dictionnaire des drogues,' 1807, and is given by this author only.

“ In rods or magdaleons.

“ In bladders, where the material continued to assume consistence. (Guibourt has thus seen a mass of 12 kg. of fresh and soft material, with a peculiar, very strong and balsamic odour.) ”

Lastly, Poncelet ("Chymie du goût," 1755) describes it "in cakes for the hard part, in phials for the liquid (balsam), and in leaves of the shrub for the average part with the consistence of thick syrup."

Two old analyses give labdanum the following compositions :—

According to Pelletier—

	Per cent.
Resin . . . . .	20.00
Gum with a little malate of lime . . . . .	0.60
Wax . . . . .	1.90
Sand, ferruginous . . . . .	72.00
Oil and loss . . . . .	1.90

According to Guibourt—

	Per cent.
Resin and oil . . . . .	86.0
Wax . . . . .	7.0
Aqueous extract . . . . .	1.0
Earthy matter and hairs . . . . .	6.0

The enormous differences apparent between these two results are not surprising, considering the very impure state in which the labdanum of commerce is marketed.

According to Parry ("Chemistry of Essential Oils," i., 503), the oleo-resin contains 0.7 to 2 per cent. of an essential oil with the following characters :—

Boiling point . . . . .	50°-185° under 15 mm.
Specific gravity . . . . .	0.928-1.011
Refractive index . . . . .	1.5100-1.5140

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It oxidises rapidly on being kept, and deposits a large quantity of crystals.

According to Masson (*Comptes Rendus*, 1912, 154, 517), this oil contains acetophenone and a second ketone of the formula  $C_9H_{16}O$ , whose constants are :—

Boiling point . . . . .	178°–179°
Specific gravity at 0° . . . . .	0.922
Optical rotation . . . . .	$\pm 0^\circ$
Refractive index at 23° . . . . .	1.4494
Melting point of the semicarbazone . . . . .	220°–221°

Masson also found in the oil extracted from the oleo-resin some alcohols, phenols, and esters, while he indicates the probable presence of guaïol.

The ketone  $C_9H_{16}O$  is trimethyl-1,5,5-hexanone-6.

The substance isolated by Emanuel, of the formula  $C_{17}H_{30}O$ , which he named ladaniol, is, according to Parry, probably an impure form of guaïol.

*Roure-Bertrand Fils* have treated a certain quantity of *Cistus ladaniferus*, gathered in the Esterel towards the end of December, and obtained, on the one hand, a gum-resin of rather soft consistence, coloured a deep green, and having a very marked balsamic odour, similar to that of the labdanum from Cyprus. On the other hand, by simple distillation and with a yield of 0.06 per cent., they obtained an essential oil of a golden yellow colour, with a very strong and not disagreeable odour.

The characters of this oil were :—

Specific gravity at 20° . . . . .	0.9033
Optical rotation at 17° . . . . .	$-12^\circ 10'$
Refractive index at 12.5° . . . . .	1.4800
Acid value . . . . .	3.7
Saponification value . . . . .	22.37
Ester value . . . . .	18.67
Solubility in 90 per cent. alcohol . . . . .	$\frac{1}{2}$ vol. to 5 vol.

The distillation waters, exhausted with petroleum ether, gave a further 0.02 per cent. of an oil of a deeper colour than the former, and whose constants were :—

Specific gravity at 17.5° . . . . .	0.9755
Optical rotation at 17° . . . . .	$-2^\circ 40'$
Acid value . . . . .	18.67
Saponification value . . . . .	41.07
Ester value . . . . .	22.40
Solubility in 90 per cent. alcohol . . . . .	$\frac{1}{2}$ vol. and over.

The latter oil had a much finer odour than the direct oil.

Owing to the small amount of raw material at their disposal, they were unable to obtain the oil of *Cistus monspeliensis*. According to *Schimmel & Co. (Bericht, October, 1903, p. 81)*, this oil has the following constants:—

Yield . . . . .	0.015 per cent.
Specific gravity at 15° . . . . .	0.9786
Optical rotation . . . . .	+ 1° 40'
Acid value . . . . .	15.7
Ester value . . . . .	31.51

It is of a clear brown colour, and between 20° and 25° deposits a considerable proportion of paraffin, melting at 64°.

**LANTANA OILS.**—*Lantana camara*, a plant of the natural order *Verbenaceæ*, is widely distributed in Java, New Caledonia, and the Philippines, and grows wild by the roadside and on waste lands throughout southern India. It is found all over Travancore up to an altitude of 4,000 feet.

According to Moudgill and Vridhachalam (*P. & E. O. R.*, 1922, 173), the plant has been introduced into India from abroad. The essential oil is pale yellow in colour, and has a pleasant aromatic odour recalling that of sage. It has been examined by Kanga (*Journal of the Institute of Science*, I., ix.), and also by *Schimmel & Co. (Report, October, 1896, and 1909)*. The most recent examination of the oil, however, is that of Moudgill and Vridhachalam (*loc. cit.*).

	Travancore oil from leaves.	Kanga's figures from leaves.	<i>Schimmel &amp; Co.'s Report, 1909.</i>
Specific gravity . . . . .	(30°/4°) 0.8842	(24°/24°) 0.92114	0.9132
Rotation . . . . .	+ 14.7	+ 1.96	+ 11.5
Refractive index . . . . .	1.4899	1.4893	1.4913
Acid value . . . . .	1.6	—	—
Saponification value . . . . .	4.6	—	—
Acetyl value . . . . .	23.4	—	—
Aldehyde content . . . . .	2.4 per cent.	—	—

The plant was collected during November. Four hundred and fifty pounds of the air-dried leaves (moisture 12.5 per cent.) were steam-distilled in a large copper still with false perforated bottom, care being taken that the leaves did not come in contact with the hot bottom of the still, and a 0.2 per cent. yield of a greenish-yellow

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oil possessing an odour which was pleasant and persistent, particularly when considerably diluted with alcohol, was obtained. It showed slight green fluorescence, and was soluble in five or more volumes of 97 per cent. alcohol.

These constants would suggest that the oil consists principally of hydrocarbons, and that it contains very small proportions of free alcohol and aldehyde. Further examination bears this out, for the oil has been found to be of comparatively simple composition, containing about 10 to 12 per cent. 1- $\alpha$ -phellandrene, 80 per cent. of a sesquiterpene much resembling caryophyllene, and the rest a complex mixture.

The oil was fractionated under reduced pressure and, finally, three fractions obtained :—

	Per cent.
(1) 55°–75° at 12 mm. . .	12 by volume
(2) 75°–125° at 12 mm. . .	8       ,,
(3) 125°–130° at 12 mm. . .	74       ,,
Residue . . .	6 (calculated by difference).

*Lantana odorata* yields an oil having an amber odour. It grows in Jamaica and other islands of the West Indies.

**LARD.**—Lard is the purified fat of the hog, *Sus scrofa*. It is used in the extraction of perfumes from flowers by the enfleurage process, and is also used in the preparation of various cosmetics. Whenever it is used, it is absolutely essential that it should be of the very finest quality and free from fatty acids. Further, it is important that free fatty acids should not develop in the fat, and in order to keep it in good condition it is often digested in the melted condition with gum benzoin, with constant stirring. The fat thus takes up benzoic acid and other constituents from the gum, and will keep sweet for a prolonged period. Lard so treated is known as “benzoated lard” or *adepts benzoatus*.

Lard, which is produced on a very large scale in the United States, is there classified as follows :—

(1) *Neutral Lard No. 1.*—This is obtained from the fat by rendering the finely cut up mass at a temperature not exceeding 50°. *Neutral lard No. 2* is similarly obtained from the fat taken only from the back of the animal.

(2) *Leaf Lard.*—The residues from which “neutral lard” has been rendered yield, when subjected to a steam heat in an autoclave, the commercial variety known as leaf lard.

(3) *Choice Kettle-rendered Lard.*—This is obtained by rendering

the residues left from the preparation of "neutral" lard in open steam jacketed vessels.

(4) *Prime Steam Lard*.—This term is applied to the fat rendered from all the other parts of the hog at steam heat.

Genuine lard for perfumery purposes should be practically neutral. It will generally have characters falling within the following limits :—

Melting point . . . . .	35°–46°
Solidifying point . . . . .	25°–30°
Saponification value . . . . .	192–199
Refractomer number . . . . .	49–52 at 40°
Iodine value . . . . .	55–66
Specific gravity $\frac{100^\circ}{15^\circ}$ . . . . .	0.860–0.863
Unsaponifiable matter . . . . .	Less than 0.5 per cent.

It should not contain more than traces of water. Care should be used in judging whether a given sample is free from cotton oil or not, since the fat of hogs which have been fed on cottonseed cake will usually give a slight reaction for cottonseed oil. There are a number of fats found in commerce under the name of lard substitutes. These are frequently mixtures of a liquid fatty oil with about 20 per cent. of the stearine of beef fat. (For the detailed examination of lard, see "Fatty Foods," Bolton and Revis, p. 101.)

**LASERPITUM OIL.**—The fruits of a species of *Laserpitium*, a genus belonging to the natural order *Umbelliferae*, yield, according to Haensel (*Chem. Zentral.*, 1906, ii., 1496), nearly 2 per cent. of a dark green essential oil having an odour recalling those of aniseed and caraway. It has a specific gravity 0.9538 at 20°; acid value, 3.2; ester value, 12.3; and ester value after acetylation, 28.5. It contains limonene, eugenol, dihydroeugenol methyl ether, and a paraffin hydrocarbon melting at 57° to 58°.

**LATHYRUS ODORATUS.**—This plant is the popular sweet pea, a member of the natural order *Leguminosae*. A small amount of the natural perfume may be found, but in the main the sweet pea perfumes of commerce are synthetic. The essential oil occurs in such minute proportions that it has never been systematically examined. It certainly contains, however, methyl anthranilate. In preparing synthetic sweet pea perfumes methyl anthranilate, benzylidene-acetone, hydroxycitronellal, and terpineol are indispensable. Numerous other synthetic perfumes are employed, and

are rounded off with natural essences, such as jasmine and bergamot.

**LAURIC ALDEHYDE.**—See “Aldehydes, Higher Fatty.”

**LAUREL-LEAF OIL.**—*Laurus nobilis*, a tree belonging to the natural order *Lauraceæ*, possesses leaves having a sharp aromatic odour. The oil, which is obtained to the extent of from 1 to 3 per cent. from these leaves, has the following characters :—

Specific gravity	0.915–0.930 (occasionally higher)
Optical rotation	— 15° to — 22°
Refractive index	1.4670–1.4775
Acid value	1.5–4
Ester value	20–53
Ester value after acetylation	36–100

The oil contains pinene, phellandrene, cineol, linalol, geraniol, eugenol, and methyl eugenol. Traces of a sesquiterpene and a sesquiterpene alcohol are also present.

**LAVENDER, OIL OF.**—As a raw material for the perfumer, the essential oil of lavender is certainly amongst the most important, both from the points of view of quality and quantity. Very large quantities are consumed in the manufacture of that typically English toilet perfume, lavender water ; a great deal is used in the equally popular eau de Cologne ; and it enters into innumerable other perfume compositions, so that its consumption is on a very large scale. France, of course, is the home of the lavender. A small amount of exceedingly fine quality is grown and distilled in England, but for all practical purposes the world's supply is produced in France. This, of course, is not quite so true of the spike lavender and its oil, since a considerable amount of this oil is produced in Spain.

So important is this oil to the perfumer, that it is of interest to trace the modern views of experts in reference to the plants from which it is actually obtained.

The position, as conceived by him, is summarised by Lamothe (“Lavand. et Spic.,” 2nd ed., 1908) as follows :—

The principal lavender species are (1) *Lavandula latifolia* (*L. spica*), also known as spike lavender, or male lavender.

(2) *Lavandula officinalis* (*L. vera*) also known as the true lavender or female lavender.

(In regard to *Lavandula latifolia*, no divergencè of opinion is to be noted.—E. J. P.)

Jordan, after a lengthy investigation, considered it necessary to classify the true lavender (*Lavandula officinalis*) into two subdivisions, namely—

(a) *Lavandula fragrans* (*lavande odorante* ; *lavande moyenne*). This variety, he stated, is widely distributed, occurring at the lower altitudes of growth.

(b) *Lavandula Delphiniensis* (*petite lavande* ; *lavande fine*). This, according to Jordan, is found exclusively in the highest regions of growth.

In addition to these, Lamothe states that there occurs a cross between *Lavandula fragrans* and *Lavandula latifolia*, which Reverchon has named *Lavandula Hybrida*, and Chatenier *Lavandula fragrans latifolia* (or *grosse lavande*, *lavande bâtard*, *lavendin*, or *spigoure*). Distillers, according to Lamothe, recognise these varieties under the names (1) *Petite lavande*, which yields the finest oil ; (2) *Lavande moyenne*, which yields a fine, but less valued oil ; and (3) *Grosse lavande*, which, being a bastard lavender, yields an inferior oil.

These views have, however, not been entirely accepted by Humbert, who in 1919–1920 examined the whole of the lavender position for the French Government, and whose considered views are the following (*vide P. & E. O. R.*, 1921, 252). He made very extensive tours through the principal lavender districts, and his long investigation and journeys have convinced him that Jordan's subdivisions of *Lavandula officinalis* into two definite varieties is incorrect. He is quite satisfied that *Lavandula officinalis*, Chaix, is a specific entity which, although subject to very great variation, gives rise in France to only one well-defined geographical race—the Pyrenean (*Lavandula pyrenaica*, D.C.). On the other hand, very important and interesting, alike from the industrial and botanical aspects, is the extreme abundance of hybrids between lavender and spike (*L. latifolia*, Vill.), particularly where the areas of the two plants come into contact. The text-books, where they do not ignore them altogether, mention these hybrids as exceptional, but the result of careful observation carried out during two summers, when natural lavender fields extending over hundreds of miles were visited, shows that hybridisation, far from being rare, takes place in nature with remarkable facility.

Spike is a native of relatively low altitudes up to 1,000 metres when facing south, and no more than 400 metres with a northern aspect, while lavender commences, broadly speaking, where spike ceases, and attains to 1,500, or even 1,800 metres above sea-level.

When either of the two species grows distinct from its ally, it presents a sum of the various distinctive characters (see *P. & E. O. R.*, June, 1921, pp. 177-178) depending on the extension or compression of the inflorescences, the size of the leaves, etc., which makes it quite easy of identification. But it is far otherwise when, ascending from the lower levels to the upper, the middle region is reached, where the areas of the two come into contact, or even overlap by encroachment; here are met, often in numbers as large as those of the pure species, plants presenting a mixture of characters which forces one to assign to them a hybrid origin. Some of the hybrids are easily distinguished, others less so (especially in herbarium specimens); these latter have remained until now almost unknown to botanists, and it is these which present the greatest danger of mixture with the plants collected for distillation—for, poor in esters and tainted with camphor, they lower considerably the linalyl acetate content of the oil, and destroy its fineness; in fact, they give an essence spike-like in character.

A consideration of the wild plants firmly establishes the specific unity of *Lavandula officinalis*, and if the hybrids with spike are objectionable from the viewpoint of the quality of the essence, it does not necessarily follow, either that lavender cannot be divided into strains or cultural races of diverse characteristics, or that crossing should, in all cases, be ruled out. On the contrary, it is probable that a careful selection may enable the separation of important lines, and that reasoned crossing with spike may produce a higher yield of oil and at the same time maintain a satisfactory quality.

It has been previously shown (*P. & E. O. R.*, 1920, p. 253) that *L. fragrans* and *L. delphiniensis*, created by Jordan at the expense of *L. officinalis*, cannot be considered as distinct species, but merely as two extreme forms of variation in accord with the local conditions of habitat. Every observation made in the course of last summer confirms this view. In all the mountains visited, without exception, from the arid chains of Provence to the high Alpine valleys, one finds the whole range of variation from one extreme to the other; from the short, squat forms with compact inflorescence, subsessile flowers, and linear-revolute leaves (*fragrans* corresponding to the most xerophil—i.e., drought-loving—adaptation: great dryness of air and soil and intense isolation), to the elongated forms with interrupted and tiered inflorescence, flowers with distinct pedicels (pedicels sometimes two-fifths of



the length of the calyx), and larger flat leaves (*delphiniensis*, the form of less arid places). Naturally, the first predominate on the south and on the dry crests of the low mountains, where the battle against extreme drought induces the morphological modifications indicated; the second to the north or in the high valleys or higher mountains, where mists and rains are less rare, or again in the shadow of the forests; the middle types are found in situations of an intermediate character; moreover, these are the most frequent. Further, one can see one type pass into the other, following variation in local conditions.

Thus the Luberon shows, on its arid brows (calcareous, of the lower Cretacean system), towards 1,000 metres high, the most xerophil forms. But on descending from the summit towards the north, one meets on the slopes, less exposed to the sun and principally towards the base, where the soil is no longer purely calcareous, but a soft Miocene formation and more hygroscopic, the whole gamut of transitions to, in the neighbourhood of ponds or rivulets, forms presenting the maximum lengthening of axes and enlargement of the leaves. The transformation of one form to the other can be proved experimentally by planting the seed of the xerophil type—or even by transplanting a growing plant—in a damper soil or climate than the original station, or *vice versa* with the other type. As to the first case, which is the more frequent (cultivation in a valley or plain of plants originally growing on dry mountains), the morphological modifications are much accentuated if the plants are put in a rich soil, and still more so if they are treated with manure. Of the same nature are the instances where a fall of rubbish has, by chance, brought about the layering of some shoots of a xerophil lavender: the layered branches may show larger leaves and tiered floral glomerules. Finally, stocks of the same type after being burnt down, give forth the following year very vigorous branches, with large leaves and floral glomerules very spaced out by the elongation of the internodes. The cause of this variation is very simple. The first shoots which form after the fire are few in number; thus they receive all the sap absorbed by the full uninjured root system, and at the same time the loss of water by transpiration and chlorovaporisation is temporarily reduced or suppressed. Hence everything occurs as if the plant grew in a humid situation—it loses the characteristics adapted to dryness; the leaves enlarge, the internodes become elongated. These first shoots are very strong; the ashes derived from the fire also contribute to their

vigour by fertilising the soil. During the following years the shoots multiply, the original conditions tend to return, and the xerophil characters reappear progressively.

When the original diagnoses of the two Jordanian species are compared, one is struck by the fact that the characters on which the author based their distinction are precisely those which are easily brought about by change of conditions, and, besides this, they are merely quantitative characters. Jordan's own words relative to *L. fragrans* are: Its appearance is very different (from that of *L. delphiniensis*); it forms denser clumps, and its stems are much tougher; the leaves all erect, narrower, and almost exactly linear, with margins turned in on the shaft, green and often rather shiny above; the flowers form denser sprays and have shorter pedicels; the calyx is shorter, more hairy, usually purplish, surrounded with oval teeth; the corolla is noticeably smaller and of a darker violet, the lobes of the lower lip very obtuse and slightly crenulated; the style is pale violet in colour; the odour of the plant is pleasant and very pronounced.

There is nothing astonishing that *L. delphiniensis* raised from seed collected in the Gap district and cultivated for seven years at Lyons should retain its characteristics in that relatively humid climate, or even that these characters should become more marked. The authentic specimens of Jordan in the herbarium of the Paris Museum show exactly the elongated inflorescence and large leaves of the less xerophil form. The museum also possesses examples of *L. fragrans* grown from Jordan's cultures. Far from presenting the extreme xerophil type, they have obviously partly lost the characters attributed to this pretended species, and are noticeably approaching the *delphiniensis* form; the leaves are already much larger, as big as in cultivated *delphiniensis*, and the inflorescences are longer and the glomerules farther apart than in many wild samples of the *delphiniensis* of Couzon, which Jordan cited as the habitat of the type of his species.

If the distinction between *L. fragrans* and *L. delphiniensis* is artificial, it is otherwise with what de Candolle called *L. pyrenaica* (*L. vera*, var. *pyrenaica*, Benthams; *L. spica*, var. *pyrenaica*, Briquet). It is not a question of the same kind of difference as between spike and lavender, but merely of a geographical race distinguished, at first glance, by the much greater size of the principal bracts; these are very large, as broad as long (6 to 9 mm. each way), almost as big as the calyx, the greater part of which they conceal; they are nearly twice as big as those of the

lavender of the Alps or Central Range, and more richly veined; they show seven to nine very prominent veins which bifurcate and anastomose towards the apex, flowers a little larger, and, because of their inclination at  $45^{\circ}$  to the principal axis, the inflorescence appears bigger. The bracteoles, as in *L. officinalis*, are very small, sublinear, and are practically invisible, as they do not pass beyond the base of the calyx. The *fragrans* and *delphinensis* types are also found in the Pyrenean variety. Specimens with white corollas and pale calices are fairly frequent among the mountain brows to the north of Villefranche-de-Conflent, in the Pyrénées-Orientales. The Pyrenean lavender is spread here and there to the exclusion of the normal type in the French and Spanish eastern Pyrenees. Just as lavender succeeds spike in altitude in the south-east, so *pyrenaica* begins where spike ceases in the Pyrenees. Further, as the district is more southern, the zone of contact is a little higher; thus in the mountains of Villefranche it occurs at about 1,200 metres altitude to the south; *L. pyrenaica* forms vast colonies, reaching almost to the summit of the mountain (1,800 metres). On the Spanish side of the border the line of contact is higher still.

*The Hybrids.*—It may appear rash, says M. Humbert, to designate as hybrids plants whose origin has not been proved experimentally by the crossing of their presumed parents. Errors have often been made by the omission of this precaution, but we have to consider that—

(1) The only possible parents are two species, because *L. Stæchas*, the third French species, being very southern, and silica borne, does not mix with the other two.

(2) The areas covered by the two presumed parents do not coincide, but only meet (or encroach a little) in a zone which corresponds to the higher limit of spike and the lower limit of lavender.

(3) In the whole of their respective areas the characters of the two species agree with those laid down.

(4) The intermediate individuals between the two species are found solely in the zone of contact, or its immediate vicinity (i.e., within a distance where insect fertilisation is practicable; the stamens being shorter than and included within the corolla tube, the action of the wind is negligible).

(5) The intermediate individuals produce seeds which are almost always sterile.

This set of circumstances, in conjunction with morphological,

biological (time of flowering), and physiological (composition of oil) indications, leaves scarcely any doubt that the origin is hybrid.

The hybrids are far from being all identical in form, but all give the odour of camphor on bruising. Some closely resemble spike in their general appearance; they are big and strong, and their flower stalks are mostly branches. Others, much commoner, are more akin to lavender; they are of more modest stature, their flower stalks are generally or entirely simple. It is these latter which are often confounded with true lavender. Besides these two types, there are others intermediate between them, some being almost exactly midway in characteristics between the two parent species. These last crosses are more easily distinguished from the parent plants. "Lavandin" is the vulgar name applied to the whole range of hybrids throughout the south-east. They flower later than lavender, but earlier than spike. The lavender-like hybrid is especially abundant in the southern Alps at altitudes of 400 to 900 metres in the vicinity of its parents; where they co-exist there is extreme danger of mixture in the lavender stills, where it is said that up to 50 per cent. weight of the charge may be hybrid. It is less common in the Causses, because contact between spike and lavender is less frequent there.

If the hybrid character of the "lavandins" is not doubtful, the exact manner in which they arise is still hypothetical. Judging from analogy, we may assume that the two principal types come from two varieties of fecundation; in one, *L. officinalis* supplies the pollen, and spike the ovule, and *vice versa*; it is the pollen-supplying parent which the offspring more resembles.

Hybrids between spike and the Pyrenean variety of lavender are less common than those between spike and the ordinary form of *L. officinalis*, not because crossing takes place with less facility in favourable circumstances, but because the points of contact between the potential parents are comparatively few owing to the fact that the *L. pyrenaica* area is less extended and much split up.

It is not necessary to pursue the question of the hybrids further here, except to say that some so-called hybrids are merely aberrant forms of either spike or lavender. Even *L. officinalis* var. *pyrenaica* has been called a hybrid, with *L. Stæchas* as a parent. This is undoubtedly wrong. The bracts of *pyrenaica* are nothing like the foliaceous sterile bracts which crown the inflorescence of *L. Stæchas*; the geographical distribution is very different: the former is a chalk-loving mountain plant, the latter affects siliceous

soil, and is purely Mediterranean; finally, *L. Stæchas* flowers in spring, and spike and lavender (ordinary and *pyrenaica*) in summer!

Complete details of the specific characters of *Lavandula officinalis* and *Lavandula latifolia* are given by M. Humbert in a report to the French National Office of Primary Vegetable Materials. (*Vide P. & E. O. R.*, 1921, 146.) Far more important, however, are the details he gives of the well-recognised hybrids of lavender and spike lavender in a similar report. (*Vide P. & E. O. R.*, 1921, 177.) The characters of these hybrids are given as follows:—

*Hybrid A.*

More resembling *L. latifolia*.

General habit and appearance of a strong *L. latifolia*, found here and there, more or less isolated, absent from many places where the potential parents co-exist, but present to the north of St. Saturnin-les-Apt at about 800 metres alt., looking south; also near Buis-les-Baronnies about 400 metres alt., north aspect; in the Nyonais; and in the Causses.

Flower stalks divergent as in *latifolia*, generally bearing in the axils of two higher leaves a pair of secondary flowering branches as developed as in *latifolia*, and making an angle of about 35° with the principal axis.

Height up to 1 metre.

Pairs of lower leaves forming, as in *latifolia*, false rosettes at the base of the flower-bearing branches, covered with whitish hairs (leaves having passed the winter), those following broader, longer, and more narrowly attenuated towards base than apex.

Bracts remaining green a long time even after flowering, at least in their upper part, recalling by their shape and venation those of *officinalis*, but relatively less broad and much more attenuated towards the apex, 5 to 7 × 3 to 4 millimetres.

Bracteoles well developed, the first two lanceolate, green at first, then brown, about half the length

*Hybrid B.*

More resembling *L. officinalis*.

General habit and appearance of *L. officinalis*, found in great abundance throughout entire zone of contact between *latifolia* and *officinalis*; often as numerous as parents.

Flower stalks more or less divergent, generally simple, but sometimes bearing in the axils of two higher leaves a pair of secondary branches.

Height variable, 30 to 80 centimetres.

Pairs of lower leaves approaching the base of the flower-bearing branches and recalling this character of *latifolia*, but false rosettes not so distinct as in that species or in hybrid A.

Bracts brown and membranous after flowering, recalling by their texture, shape and venation those of *officinalis*, but rather less wide and a little more attenuated towards the apex, 3 to 5 × 2 to 3 millimetres.

Bracteoles well developed, brownish, the first two lanceolate, from  $\frac{2}{3}$  to  $\frac{1}{2}$  as long as the bracts,

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of the bracts, from each side of which they diverge very distinctly, and extending beyond the base of the calyx; those following smaller.

Calyx almost intermediate in downiness and general appearance between that of *officinalis* and that of *latifolia*, or more resembling the former.

Corolla intermediate in shape, its upper lip a little less full than in *officinalis*.

Flowers inclined at about 35° to the principal axis.

Principal inflorescence very bushy, often exceeding 10 centimetres in length, more or less interrupted at the base, about 6 to 12 flowers in the axil of each bract (cyme or half glomerule).

*Characters common to both Hybrids.*—Flowering beginning later than in *officinalis* and earlier than in *latifolia* in the same situation.

Seeds almost always sterile.

Odour camphoraceous on bruising.

*Hybrids of L. officinalis var. pyrenaica and L. latifolia.*—These hybrids are of two types corresponding to those described above. The name *L. aurigeriana* has been given to a form more closely resembling *pyrenaica* than *latifolia*, the homologue, therefore, of hybrid B. This is, as with ordinary *officinalis* hybrids, the more frequent. It is distinguished from *pyrenaica*, as its homologue is from *officinalis*, more particularly by the great development of the bracteoles, the reduction of the larger bracts, and the odour of camphor. Its characters are: flower stalks more or less divergent, simple, sometimes some branching (30 to 60 centimetres long); lower leaves small, sublinear, or more or less spatulate, whitish, compact, those following larger, fully green, broader, more attenuated towards base than apex; bracts membranous, brownish, one-third longer than wide (6 to 7 × 4 to 4.5 millimetres), usually with seven principal veins, forking and anastomosing towards the apex; bracteoles of the first order, large, lanceolate, half (or rather more) as long as the bracts, divergent, conspicuous, those following about half as long, sublinear; upper lip of corolla less full than in *pyrenaica*; inflorescence not usually interrupted, but loose (3 to 4 centimetres long) and slender; flowering beginning later than with *pyrenaica*, but earlier than with spike, in the same situation;

from each side of which they appear distinctly, divergent, appreciably extending beyond the base of the calyx; those following small and hardly visible.

Calyx almost intermediate between *officinalis* and *latifolia*, or more resembling the latter.

Corolla intermediate between those of the two parents.

As A.

Inflorescence slender, 1.5 to 6 centimetres long, usually not interrupted, 1 to 5 flowers in the axil of each bract (cyme or half glomerule).

seeds almost always sterile ; odour camphoraceous on bruising. *L. aurigeriana* is distinguished from hybrid B by the large size of its bracts ; in both cases they are of the same shape and texture, but here they are more developed and more richly veined—the bracts of the Pyrenean hybrid are to those of the Alpine hybrid as the bracts of *L. pyrenaica* are to those of *L. officinalis*.

Side by side with the forms more allied to *L. pyrenaica* are found (but more rarely) forms tending more towards *L. latifolia* ; either by the bracts remaining green and herbaceous a longer time or by having more branched flower stalks and wider and more or less spatulate leaves, or by a longer and more compact inflorescence, often broken at the base ; all these characters can co-exist, and in that case the hybrid may clearly be described as *latifolia-pyrenaica* rather than *pyrenaica-latifolia*. When the influence of *L. latifolia* predominates, it becomes almost impossible to distinguish the hybrid morphologically from its homologue *L. latifolia-officinalis*.

The chief importance of the above considerations from a practical point of view amount to this. Certain types of the true lavender plant yield essential oils of better odour value than others. But in every instance hybridisation lowers the value of the oil, since it reduces the ester value without any corresponding compensation. It is true that the determination of the ester value is no criterion of the value of oils growing in different districts, but where the cause of the reduction in ester value is hybridisation, the ester value is a much more definite factor in the valuation of the oil. In regard to the distillation of lavender oil, one has to take two principal factors into account. It is, of course, advantageous to use steam distillation if possible. This is, however, only possible where the supply of flowers available at the place of distillation is sufficient to justify the erection of steam stills. By direct steam distillation the flowers are not sodden with water, and a large volume of steam can pass through them in the minimum of time. The operation, therefore, proceeds very rapidly with a minimum decomposition of esters into free alcohols and free acids. But it should not be forgotten that steam carries over a certain amount of resinous matter, which accounts for the fact that high ester oils are often less soluble in 70 per cent. alcohol than low ester oils. In districts far removed from towns distillation must of necessity be carried on by means of portable direct-fire stills, in which, however great care is used, burning of the flowers and decomposition of the esters is inevitable.

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The characters of the various oils of lavender, those derived from the true lavender, the spike lavender, and species of lavender not hitherto considered, may now be examined.

It must be remembered that, apart from questions of hybridisation, the characters of the actually true lavender oil will vary with the locality in which the plant is grown. It is, of course, also true that as the gatherers of the uncultivated lavender approach the zone of altitudes where the true lavender and the spike lavender meet, various types of hybrids will be gathered with the true lavender, and this will affect the characters of the commercial oil obtained from the plants so cut. The general characters assigned to pure French lavender oil must, of course, be taken to allow for this latter consideration.

A normal French lavender oil will be found to have characters which fall within the following limits :—

Specific gravity	. . . . .	0.882–0.900
Optical rotation	. . . . .	–3° to 10° (rarely below – 5°)
Acid value	. . . . .	0 to 1
Esters as linalyl acetate	. . . . .	28–42 per cent. (rarely up to 55 per cent.)
Solubility in 70 per cent. alcohol at 20°	1 in 3	

Oils distilled from plants grown on the Italian frontier will, in general, correspond with these values, except that the ester value will vary from 20 to 30 per cent. The presence of bastard lavender oils, or lavandin oils as they are usually called, will alter these values proportionately. Lavandin oils will usually have a specific gravity of from 0.900 to 0.905, and the ester content may fall as low as 6 per cent.

English lavender oil differs very materially in most respects from French oil. The industry is quite small compared with the French lavender industry, and whilst the wild plant is mostly used in France, in England only the cultivated plant is distilled. The lavender plantations in England are confined almost entirely to Mitcham, Reigate, Carshalton, Beddington, Wallington, Canterbury, and Hitchin, with a few fields in other localities. English lavender oil, which has an exceedingly fine odour, and which is always considerably more expensive than French lavender oil, has the following characters :—

Specific gravity	. . . . .	0.884–0.898
Optical rotation	. . . . .	– 4° to – 10°
Esters	. . . . .	7–11 per cent.



If kept for any lengthy period the oil resinifies, and these limit figures are exceeded.

For all practical purposes, French and English lavender oils are the only true lavender oils used commercially. Spanish so-called lavender oil is a mixture distilled from various species of labiate plants, and to-day, except as spike lavender oil, no lavender oil is exported from Spain. Before passing on to spike lavender oil, it will be of interest to consider the essential oils distilled from entirely different species of lavender.

*Lavandula dentata* is a plant which grows in Spain, Morocco, and Algeria. It yields an essential oil whose odour recalls those of rosemary and camphor. It is doubtful whether the flowers are ever distilled alone, as in Spain the plant grows in close proximity with other related plants, and they are usually cut indiscriminately. So far as can be recorded, the oil has the following characters :—

Specific gravity	.	.	.	0.942–0.963
Optical rotation	.	.	.	+ 30° to + 42°
Refractive index	.	.	.	1.4700–1.4800
Acid value	.	.	.	About 6
Ester value	.	.	.	12–25

*Lavandula Stœchas*.—This plant is known in Spain as *Romero Santo*, the holy rosemary. *Schimmel & Co.* examined an oil which they believed to be that of *Lavandula Stœchas*, and described it as having the following characters :—

Specific gravity	.	.	.	0.9317
Optical rotation	.	.	.	– 39° 40'
Refractive index	.	.	.	1.47099
Esters	.	.	.	35.6 per cent.

*Roure-Bertrand Fils*, however (*Bulletin*, October, 1921, 3), have examined authentic specimens, and they give the following figures for the oil, contending that *Schimmel's* oil cannot be that of *Lavandula Stœchas* :—

Specific gravity	.	.	.	0.945–0.962
Optical rotation	.	.	.	+ 35° 30' to + 47°
Ester value	.	.	.	13.1–17.74
Ester value after acetylation	.	.	.	47

The principal constituents are *dextro*-camphor and *dextro*-fenchone. Terpeneol, fenchyl alcohol, and a phenol are probably present.

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*Lavandula pedunculata* is found growing in Portugal, and yields an oil of not very pleasant odour. It has a specific gravity 0.939, optical rotation  $-44^{\circ} 54'$ , and contains about 39 per cent. of esters of unknown characters.

*Lavandula Burmanni*.—Samples of the essential oil of this plant, grown in India, have been examined by *Schimmel & Co.* (*Bericht*, October, 1913, 110). One oil was distilled from the leaves, and was of a yellow colour and had a lemongrass type of odour. The other was a light brown oil, distilled from the flowers, and had a distinct fenchone odour. Specimens of both oils have also been examined at the Indian Institute of Science at Bangalore. The two oils have the following characters :—

	Leaf oil.	Flower oil.
Specific gravity . . . .	0.895–0.913	0.921 to 0.931
Optical rotation . . . .	$-0^{\circ} 40'$	$+1^{\circ} 40'$
Acid value . . . . .	10	1.9
Ester value . . . . .	36–44	115–150
Refractive index at $25^{\circ}$ . . . .	1.4830	1.4683

Pellini (*Ann. di Chim. Applic.*, vii., 3) has examined samples of Sicilian lavender oil which he considers to be the distillate of some form of *Lavandula vera*. The botanical origin of the plants, however, requires verification. The oil has the following characters :—

Specific gravity . . . . .	0.884–0.8907
Optical rotation . . . . .	$-4^{\circ} 54'$ to $-5^{\circ} 43'$
Refractive index at $25^{\circ}$ . . . .	1.4636–1.4674
Esters . . . . .	6.5–13.16 per cent.

French lavender oil, from *Lavandula officinalis*, contains as its principal constituent the ester linalyl acetate. There are also present linalyl butyrate, valerianate, and caproate. Free linalol is also present, as is also, probably, free geraniol. Pinene, limonene, and a sesquiterpene are also present. Coumarin, furfurol, amyl alcohol, ethyl-amyl-ketone, and *dextro*-borneol are present in traces, and probably cineol and valeric aldehyde.

The principal difference between French and English oil is the lower content of ester and the higher amount of cineol in the latter.

The following is abstracted from the report on lavender oil

presented to the Lavender Congress held at Digne in 1921 by *Roure-Bertrand Fils* :—

### FRENCH OIL OF LAVENDER

*Distillation.*—In considering the distillation of lavender, two cases have to be borne in mind :—

(1) Where the quantity treated is important enough to allow the use of a steam distillation plant.

(2) Where the quantity only warrants the employment of a naked-fire still.

In the first case the distillation can be effected either by direct steam or by the use of a false bottom. The oil obtained by direct steam distillation, although a little less soluble than that from a false bottom apparatus, is much richer in esters, and the yield is at least equal in quantity. Further, the yield is very variable, ranging from 0.6 to 1.2 per cent.

In the second case, the oil obtained is very much the same as the distillate from the false-bottomed stills. Its ester content is lower than that of oils obtained by direct steam distillation, but it is more soluble.

These results can be very easily explained.

By direct steam distillation the flowers are not soaked with water, and it is possible to pass a large quantity of vapour through the mass in a fixed time. Owing to this, the operation proceeds very rapidly, avoiding thereby the saponification of the esters. On the other hand, the steam carries over a certain amount of resinous matter which reduces the solubility of the oil in alcohol.

In false-bottom distillation it is necessary to wet the flowers with a certain quantity of water, which retards distillation. Indeed, if ebullition is too vigorous, the liquid emulsifies, fills the whole of the apparatus, and there is a danger of it invading the serpentine. Further, the prolonged contact of the flowers with water favours the saponification of the esters, which explains the low content observed.

This inconvenience is also found in distilling by naked fire, and it is often aggravated because the plant becomes scorched by the flames which lick the still. We shall return elsewhere to this subject when we deal with this process of distillation, which is particularly interesting to the distillers in the mountains.

As regards steam distillation apparatus, the question arises as to the employment of medium or low-pressure boilers. In our opinion, the results with pressures up to 7 kg. are the same.

With a pressure of 7 kg. and under the usual condition of distillation, one cannot obtain a reduction of the pressure of the superheated steam in a still which has not been carefully calorifuged. The only matter of importance, then, is to have a boiler sufficiently large to generate the necessary quantity of steam. It is evident that with higher pressures—or, better still, with boilers having superheaters, distillation can be carried on with absolutely dry and superheated steam. In this case one has undoubtedly an even more rapid distillation; but the oil may suffer from the superheated steam and from the fact that bodies not carried over at 100° are carried over by the superheated steam.

Is it possible to improve distillation where a naked-fire still is inevitable?

It is evident that, by placing in the alembic a grill sufficiently high that the boiling water cannot touch it, and that by constructing a furnace in such a manner that the flames cannot reach the portions above the water, results can be obtained reasonably the same as by the employment of direct steam. In short, one can increase the rapidity of distillation and the flowers are not sodden.

However, it would seem to be difficult to modify those small portable stills which are usually placed on a furnace consisting of a few stones. But if the water soaks the flowers, and if the flame operates on parts which are not damped, it is impossible to distil quickly, and a large part of the esters is always decomposed. This consequence appears to us inevitable.

Where water for cooling is scanty, it is very important to restrict the quantity used as much as possible, and different methods have been devised to this end.

By the use of air condensers of sufficient size, all the vapour coming from the still can be condensed, and by avoiding excess of surface the water from the condensed vapour can be passed into a water cooler for complete refrigeration. In these circumstances the water required is reduced to about a sixth.

To diminish the importance of the aero-condenser, one can spray with cold water; the water evaporating from the condenser absorbs considerable heat, and thus allows the use of an apparatus of moderate dimensions. Unfortunately, these condensers have the disadvantage of corroding very quickly.

Finally, to diminish still further the water necessary for condensation, it can be recovered and cooled by letting it drop on well-ventilated fascines. Part of the water evaporates and the

remainder is cooled very rapidly. This involves a system of pumps to raise the water and to return it to the cooler.

These various methods of cooling only appear applicable to those works which have to be set up in districts where water is scarce ; but one cannot really adapt them to movable plant of little importance. For such, the best means of economising water is to employ suitable non-corrosive refrigerators.

*Recovery of Oil from the Waters.*—It seems to us that too much importance has been given to this matter, particularly at the moment.

We shall not examine here the oil contained in the distillation waters ; it will suffice to say that this oil is of a special nature and nothing like the direct oil, as regards either odour or characteristics. It has a low ester content, rarely exceeding 6 to 7 per cent. ; its odour does not approach that of the direct, but it is not, however, disagreeable. On the other hand, it is very soluble in alcohol.

During a number of experiments on recovery, we have not been able to obtain more than an average of 500 to 750 grams of oil from 1,000 litres of water. The processes employed were either redistillation or exhaustion with petroleum ether. According to certain authors a kilogramme of essence can be obtained by the distillation of 400 litres of the mother liquor. The figure appears to us to be unreasonable, and we believe it is obtained by working on the 400 litres which constitute the head of the distillation of about 2,000 litres of mother liquor, the essence in solution passing really with the first 400 litres.

Redistillation of waters is the most practical method of recovering the oil. The cost of recovery (taking no account of the value of the waters themselves) depends on the price of charcoal and labour, and would be about 10 to 15 francs with charcoal at about 150 francs per ton.

This recovered essence should not, in our opinion, be mixed with the direct oil, for not only does it modify the odour, but it lowers the ester content very materially. We venture to add, however, that it would be advisable to recover this oil, if only to replace spike, with those distillers who have the bad habit of adding spike to their lavender.

To sum up, we consider that the recovery of oil from mother waters is not profitable when flowers are cheap and charcoal is dear.

*Constitution.*—French lavender oil is a pale yellow liquid, of

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which the principal constituent is linalyl acetate in the proportion of 30 to 60 per cent., besides a little geranyl acetate, free linalol and geraniol, and of the butyric, capric and valerianic esters of these alcohols.

Among the hydrocarbons which have been isolated, limonene, caryophyllene and a little *d*-pinene have been identified.

Besides these constituents, which together represent the greater part of the oil, traces of coumarin have been found, and very small quantities of the following compounds: furfurol, valerianic aldehyde, amyl alcohol, ethyl-amyl-ketone, and *d*-borneol.

Nerol and thymol have also been stated as components of lavender, but the presence of the last appears doubtful.

Cineol is met with as one of the principal constituents of English lavender oil, where it occurs in the proportion of 5 to 10 per cent. It is not present in the French oil.

Without definitely denying the presence of bodies other than the foregoing in French oil, it may be said without fear of contradiction that if an essence shows distinctly the presence of any other constituent, it is not natural and certainly contains a fraudulent addition.

*Analytical Characters.*—When the analytical characters of an oil have been determined after the examination of thousands of samples from various sources carried out by different chemists, these characters may be regarded as normal and as establishing limits of variation which may be regarded as fixed.

This is the case with French lavender oil. From our own observations we put these limits at the following:—

Specific gravity at 15°	0.882–0.897
	(Generally from 0.886–0.895)
Optical rotation at 15°	– 3° to – 10°
	(Generally from – 4° to – 8°)
Acid value	0–0.9
Saponification number	80–170
„ after acetylation	160–200
Esters calculated as linalyl acetate	28–60 per cent.
Solubility at 20° in 70 per cent. alcohol	1–3 vol.
(Sometimes with slight opalescence with oils of a high ester value.)	

A clear solution should not become turbid on the further addition of alcohol.

It is only after personal observation that we indicate 0.897 as the maximum limit of specific gravity. We have, in fact, noted an oil of our own distillation which had this specific gravity and

which was otherwise of the first quality. However, it must be remembered that this limit is exceptional, and that generally the specific gravity of French oil lies between 0.886 and 0.895. Similarly the optical rotation varies as a rule between  $-4^{\circ}$  and  $-8^{\circ}$ . On the other hand, the limit we give for the acid value has never been exceeded, and is rarely reached by an oil of recent manufacture.

Supplemental to the particulars regarding French lavender oil, we give below the characters of the Italian oil.

Specific gravity at $15^{\circ}$	0.882-0.887
Optical rotation at $15^{\circ}$	$-6^{\circ}$ to $-9^{\circ} 30'$
Ester content	20-29 per cent.
Solubility in 65 per cent. alcohol	2 in 4 vol. and more.

As will be seen, this oil is lighter and much more soluble than French essence. But its ester content is noticeably lower.

*Valuation of the Oils.*—No oil exists which has afforded so much fuel for discussion as lavender oil. Every country and every district claims to produce the best; and we have joined many times, and have no doubt shall participate again in delusive and, in our opinion, utterly useless discussions.

The question as to the esters is invariably the starting point of these discussions. Should lavender oil be valued according to its ester content?

The following is our reply to this capital question:—

Lavender oil, being above everything a perfumery material, in the first place should be tested by the nose; not a cursory but a systematic examination, which eight times out of ten will show whether a lavender oil has been falsified by any of the usual means. Especially is this the case where the adulterant is an oil of a highly camphoraceous odour, such as spike, or even more so with turpentine. We never carry out a chemical analysis of an oil without at the same time testing its odour on volatilisation, and it is only when this olfactory examination is complete that we take account of the characters determined by analysis. That being so, we are firmly convinced that the richer a lavender oil is in esters, the better it is as regards fineness, sweetness and, above all, "body," and consequently perfume value. We hasten to add that there are exceptions to this, but only very rare ones.

Undoubtedly, there are excellent essences, titrating barely 30 per cent. esters. The Italian oils are a case in point, but when one compares these with oils showing 50 to 55 per cent., one is

forced to recognise that the ester content is a predominating factor in the valuation of lavender oils. This principle having been accepted by most buyers of lavender, it has led, unhappily, to a system of fraud by means of artificial esters, and only this year 40 per cent. of the samples analysed in our laboratory have been proved to be adulterated.

We shall later on go more fully into this question of adulteration and the methods of detection. At the moment we will remark that it is not alone sufficient for an oil to possess a high ester content. It is also necessary that the other characteristics should be examined and that they should come within the limits indicated above.

As the valuation of lavender oil is based on the ester content, this constant soon overshadowed all the others ; and sophistication by means of artificial esters, as we have already said, is practised without any regard to the density, optical rotation, and even, sometimes, the solubility.

On this point the keenness of adulterators has been such that lavenders showing more than 100 per cent. of esters calculated as  $\text{CH}_3\text{.COO.C}_{10}\text{H}_{17}$  may be analysed. This can be explained by the molecular weights or the basicity of the acid.

A higher ester content than 60 per cent. is never seen, and the best oils usually titrate between 40 and 58 per cent. A content as low as 28 per cent. may be passed, this corresponding very closely to the maximum content of Italian oils. These latter, however, possess a comparatively low density, while French oils of low titration have usually a high specific gravity. That comes very often from distilling lavender and spike together or, more simply still, by the fraudulent addition of spike oil.

Nevertheless, it is fair to say that a sample of French oil entirely from lavender gathered at a low altitude possessed a poor ester content, but at the same time its density was lower and the odour far from being spike-like, thus distinguishing it from fraudulent oils.

Formerly lavender oils were adulterated with terpinyl acetate or glycerin triacetate, but these additions were so easily detected that adulterators now resort to more subtle methods, and new bodies, the cost of which had put them out of reach hitherto, became very numerous as the price for the oil advanced. We may add that the small mountain distiller would have some difficulty in procuring the adulterants in question, but individuals sought him out and brought them to his notice, showed him the way to



use them, and gave him the false assurance that the addition would not be discovered.

We find at the present moment oils adulterated with a whole gamut of fatty esters, principally decylic ester, ethyl caproate, and methyl laurate. In addition, succinates, oxalates, phthalates, etc., have been found, and, in spite of the wondrous slinness and astuteness of the sophisticators, every adulterant has been recognised, and we will show later on the surest methods of detecting frauds.

Linalyl acetate alone could, within limits, be used as an adulterant without raising suspicion. But its price being higher than lavender, we are spared this eventuality.

*Research for Adulterants.*—It would be superfluous to attempt to detect chemically all the adulterants of lavender oil. It is clear that odour alone suffices to recognise many of them. Such is the case with oils of spike, rosemary, and sage, but it is possible to reveal their presence by the detection of camphor, which is not a constituent of lavender. Nevertheless, when the quantity of an adulterant is important, it is unusual for its presence not to be shown by a simple examination of the analytical factors. We have brought out this fact in our consecutive study of the constants.

Beyond those adulterants the composition and odour of which appreciably resemble lavender, there exist some much more elusive, either because of being employed in small quantities to correct certain figures modified by another adulterant, or because their odour passes unnoticed. However, at present we can detect all known adulterants, and we give below the best means of recognising the chief sophistications.

*Oil of Turpentine.*—Its presence is often recognised by its odour. From the point of view of physical characters, it lowers the specific gravity and, above all, the solubility. Being laevorotatory, it increases the optical rotation, as French oil is always employed.

Lavender oil contains but little pinene, which is the chief constituent of turpentine oil. The presence of turpentine is easily demonstrated by the identification of the pinene in those fractions distilling at about 160°. To identify the pinene, it is converted into nitrosochloride.

Fifty grams of the suspected fraction is mixed with 50 grams of amyl nitrite. The mixture is cooled and 15 c.c. of 33 per cent. hydrochloric acid added gradually. The nitrosochloride crystallises after a short time in the form of little white tablets which,

when purified by recrystallisation, melt at about  $103^{\circ}$ . When the yield of nitrosochloride is less than the optical rotation of the pinene would indicate, conversion into *pinonic acid* should be effected.

One hundred grams of the suspected fraction are shaken with 233 grams of potassium permanganate in 3 litres of water and cooled over ice. The portion not entering into the reaction is decanted; the neutral products are removed by ether, and finally a little sulphuric acid is added to liberate the pinonic acid. This is identified by its semicarbazone, melting point  $204^{\circ}$ .

*Oils of Cedar and Gurjun.*—These adulterants are, broadly, used to bring within the normal limits of optical rotation an oil which has been modified by the addition of another adulterant. Cedar oil is easily recognised by its smell, gurjun oil much less so. But both have a very high density and a very poor solubility. For the detection of either adulterant one especially considers the fraction of the oil boiling about  $260^{\circ}$ . This portion is oxidised with potassium permanganate, and when cedar oil is present the cedrene is converted into a glycol,  $C_{15}H_{26}O_2$ , melting at  $160^{\circ}$ . In the case of gurjun, the product of oxidation in acetone solution contains a fraction boiling between  $170^{\circ}$  and  $180^{\circ}$  under 12 mm., and yields a semicarbazone melting at  $234^{\circ}$ .

*Alcohol.*—Ethyl alcohol has sometimes been met as a lavender adulterant. Its effect is to lower the density and improve the solubility. Its presence is easily detected by allowing the oil to fall, drop by drop, into water; the drops, instead of remaining clear, as is the case with pure oils, become opaque and milky.

To detect alcohol chemically, the oil is very slowly distilled, and the first drops coming over are collected and passed through a moistened filter to remove the drops of oil carried over. The clear solution is then made alkaline with potash, heated to  $50^{\circ}$  to  $60^{\circ}$ , and a solution of iodine in potassium iodide added up to the formation of a persistent yellow coloration. The presence of alcohol is shown by the precipitation, after a time, of crystalline iodoform, recognised especially by its odour. It should be noted that aldehydes, acetone, and acetic ether give the same reaction.

When the quantity of alcohol is sufficiently large, the oil may be shaken with water and glycerine. The reduction in the volume of the oil shows the quantity of added alcohol. This quantity can

also be determined from the density of the oil before and after shaking with the water, and if

D represents the density of the oil at 15°,

d represents the density at 15° after shaking,

p the specific gravity of the alcohol,

then the percentage amount of alcohol is given by the formula

$$\frac{(d - D)100}{d - p}.$$

A more delicate method for determining the alcohol content consists in ascertaining the methyl value of the oil; this should be *nil* for a pure essence.

It is unnecessary to add that this process is valueless if the oil contains fraudulently-added ethyl or methyl esters.

*Resin.*—The addition of resin is easily recognised by the increase in the acid value, specific gravity, and viscosity, and especially by the residue after evaporation, which, for a pure oil, should not exceed a maximum of 4 per cent. The determination of the saponification number of this residue will indicate the nature of the resin used.

*Benzoic and Salicylic Acids.*—Both these acids have been often employed as adulterants of lavender to raise the apparent saponification number. They do not affect the specific gravity or the solubility, and only a high acid value leads their presence to be suspected. They may be detected as follows:—

The suspected essence is shaken with a weak solution of sodium carbonate and then decanted. The aqueous solution is acidulated with dilute sulphuric acid, exhausted with ether, and the ethereal solution is evaporated. The residue is composed of the free acids of the assayed oil, and benzoic acid can be easily isolated in a pure state by sublimation in the form of needles melting at 120°. Salicylic acid is easily identified by the violet coloration formed with ferric chloride and by its conversion into methyl salicylate.

*Examination for Artificial Esters.*—The importance of the ester content of lavender oils being admitted, it is among the artificial esters that the principal and most damaging adulterants are found. For the detection two groups of esters must be considered, those like the acetates or terpinyl and glyceryl, in which the acid is very volatile, and those, such as oxalates, tartrates, citrates, laurates, caproates, etc., where the acid is, on the contrary, only of slight volatility.

## PERFUMERY

*Terpinyl Acetate*.—Below we give a very simple method of easily detecting this ester, which was formerly used on a large scale for the adulteration of lavender.

The saponification of pure linalyl acetate by a seminormal alcoholic solution of potash is complete at the end of a quarter of an hour on the water bath, while terpinyl acetate requires a very long time. A fractional saponification will thus demonstrate the presence of this ester. For that purpose, the saponification number is determined at the end of half an hour and at the end of one hour. If the oil is pure, the two figures will be practically identical, and if, on the contrary, a difference exists, the presence of terpinyl acetate may be deduced.

For 5, 10, and 23 per cent. of terpinyl acetate, differences between the two saponification numbers of 3.5, 5.5, and 10.9 respectively have been found.

*Glyceryl Triacetate (Triacetin)*.—The examination for this ester is based on its high solubility in water and low solubility in alcoholic solutions. Ten cubic centimetres of oil are exhausted with 20 c.c. of 5 per cent. alcohol. After standing, the clear solution is filtered and exactly neutralised in the presence of phenolphthalein. It is then saponified for one hour by means of 5 c.c. of seminormal solution, and the quantity of potash absorbed is noted. For pure oils this quantity never exceeds 0.1 c.c., and the addition of 1 per cent. of triacetin will increase this to 0.5 c.c. If a larger quantity of oil is available, the ester may be isolated by exhaustion with weak alcohol and the acetic acid and glycerine identified.

*Esters of slightly volatile Acids*.—Among the esters intended to raise the ester content of lavender, succinates, oxalates, tartrates, and phthalates were early exposed. Then, these having been recognised, the adulterators especially used decylic ether and ethyl caproate. Finally, during the last few months we have discovered a new fraud by means of methyl laurate.

All these esters of slightly volatile acids are detected in the same manner, and one can easily detect them by chemical means when the smell has not already revealed their presence. The latter is particularly easy with decylic ether and methyl laurate.

The method of investigation is so much more delicate that it does not involve the use of more oil than in the determination of the saponification number; in fact, when this index is determined, the contents of the flask are evaporated to dryness after the addition of a few drops of potash solution. The residue is dissolved

in 5 to 10 c.c. of water and the solution is decomposed with dilute sulphuric acid. The acids are then freed, and there is passed through the flask a current of steam sufficiently strong to carry over 250 c.c. of liquid within half an hour, the contents of the flask being maintained by means of a small flame at about 10 c.c. In principle, the 250 c.c. distilled contain all the acids. However, as a precaution, a further 100 c.c. of liquid should be distilled.

This operation completed, the acid value of the 250 c.c. is estimated in the ordinary way with phenolphthalein as indicator, and to this figure is added that of the 100 c.c., which is never above 0.2 if the operation has been well managed. If the oil is pure, all the acids should be found in the distillates, and consequently the *total acid value* should be equal to the saponification number. In practice, the *total acid value* is lower, *but with a pure essence it should never differ from the saponification number by more than 3*. When the oil examined contains esters of slightly volatile acids, these acids remain in the flask (where they can be identified), and the more of them there are the greater is the difference between the total acid value and the saponification number.

We have examined in the above manner the influence of decylic ester on lavender oil, and have obtained the following results:—

	Saponi- fication number.	Total acid value.	Difference.
Pure oil, our distillation	155.13	154.00	1.13
„ + 2.5 per cent. decylic ester	157.00	153.00	4.00
„ + 5 „ „	158.77	149.33	9.44
„ + 10 „ „	162.46	140.00	22.46

By this process the presence of less than 3 per cent. of decylic ester can be recognised, and, starting from this point, the addition of 1 per cent. of the ester increases the difference by about 2.

Spike lavender oil is also of the very highest importance to the perfumer, and, being far cheaper than lavender oil, allows the employment of a perfume with some of the characteristics of true lavender oil to be used in cheap compositions. The finest spike lavender oil is distilled in France, but a very large amount is now distilled in Spain. The Spanish oil, although of excellent quality, is inferior in character to the French oil, probably because the true

spike lavender grows in company with other lavender species in Spain and the cuttings are made without any differentiation between the species.

*Lavandula latifolia*, the spike lavender, grows in France, freely in La Basse, Provence, and Languedoc; in Spain, in northern Africa, and to some extent in Italy. It is, in France, usually called "male" lavender. The plant and its essential oil have a much more camphoraceous odour than the true lavender. The French output amounts to about 25,000 kg. per annum, and it is distilled in Drôme, Vaucluse, Basses-Alpes, Bouches du Rhône, Var, Alpes-Maritimes, Gard, Herault, Aude and other departments. In Spain the oil is distilled in the provinces of Granada, Valencia, Murcia, and Cordoba. The oil, which is known in Spain as *Espliego*, is produced to the extent of from 50,000 to 60,000 kg. per annum, and finds its way, either direct or sometimes *via* France, to the consuming markets. It was originally introduced as "lavender oil," and considerable doubt was expressed as to its botanical origin. Its quality has varied considerably, and it is probable that no great amount of care is exercised in gathering the flowers, and that some admixture with different species takes place. A Spanish spike oil may be regarded as pure, or at most mixed with closely allied labiate oils, if its characters fall within the following limits :—

Specific gravity	. . . . .	0.902–0.916
Optical rotation	. . . . .	+ 4° to – 6°
Refractive index	. . . . .	1.4615–1.4670
Borneol	. . . . .	30–44 per cent.
Esters, as bornyl acetate	. . . . .	1–6 „
Solubility in 70 per cent. alcohol	. . . . .	1 in 3

Any important admixture with sage oil, which is usually due to indiscriminate cutting of plants, is indicated by decreased solubility and a lowering of the borneol content.

The writer (E. J. P.) and C. T. Bennett have recently examined a sample of adulterated Spanish spike lavender oil which appeared to contain some fraction of camphor oil (*La Parfumerie Moderne*, 1924, 150).

The sample had the following characters :—

Specific gravity	. . . . .	0.9315
Optical rotation	. . . . .	– 1° 15'
Refractive index at 20°.	. . . . .	1.4756
Total alcohols (as borneol)	. . . . .	34.9 per cent.
Esters as bornyl acetate	. . . . .	2.8 „

# P E R F U M E R Y

Two samples of pure oils were examined for the purpose of comparison. These samples had the following characters:—

	A.	B.
Specific gravity . . .	0.906 ..	0.914
Optical rotation . . .	— 2° ..	— 0° 15'
Refractive index at 20° . .	1.4650 ..	1.4683
Total alcohols as borneol .	31.1 per cent. ..	31.7 per cent.
Esters as bornyl acetate .	2.8 „ ..	5.1 „

The three samples were fractionally distilled under reduced pressure, the fractions being collected as follows: the first 10 per cent., then four fractions of 20 per cent., and residue 10 per cent.

The following were the results of these fractional distillations:—

## *Fractions from Oil A*

	1 10 per cent.	2 20 per cent.	3 20 per cent.
Specific gravity .	0.904	0.904	0.904
Optical rotation .	+ 4°	+ 2° 30'	Nil
Refractive index .	1.4610	1.4618	1.4630

	4 20 per cent.	5 20 per cent.	6 10 per cent. residue.
Specific gravity .	0.901	0.901	0.917
Optical rotation .	— 2°	— 3°	Too dark
Refractive index .	1.4642	1.4672	1.4864

## *Fractions from Oil B*

	1 10 per cent.	2 20 per cent.	3 20 per cent.
Specific gravity .	0.900	0.900	0.905
Optical rotation .	— 1° 30'	— 1°	Slightly +
Refractive index .	1.4650	1.4645	1.4650

# P E R F U M E R Y

	4 20 per cent.	5 20 per cent.	6 10 per cent. residue.
Specific gravity .	0.910	0.919	0.946
Optical rotation .	Slightly +	Slightly +	Too dark
Refractive index .	1.4670	1.4705	1.4850

## *Fractions from Adulterated Oil*

	1 10 per cent.	2 20 per cent.	3 20 per cent.
Specific gravity .	0.898	0.906	0.918
Optical rotation .	+ 4°	+ 3°	+ 1°
Refractive index .	1.4655	1.4660	1.4695

	4 20 per cent.	5 20 per cent.	6 10 per cent. residue.
Specific gravity .	0.931	0.946	0.962
Optical rotation .	— 1°	— 1°	Too dark
Refractive index .	1.4745	1.4815	1.4925

This last fraction had a distinct odour of safrol.

The odour of the adulterated oil indicated the presence of some abnormal constituent, but nothing definite was suggested thereby.

The high specific gravity and high refractive index of the successive fractions of the suspected oil, compared with the corresponding figures for the pure oils, clearly indicated the presence of an abnormally high-boiling constituent of high specific gravity and high refractive index, such as one would expect to find in certain fractions of camphor oil.

The last fractions of the suspected sample and of sample B were again fractionated under greatly reduced pressure, at about 20 mm.

Fractions 4 and 5 were mixed and refractionated into four



fractions, each representing 10 per cent. of the original oil. The last of these four fractions had the following characters :—

	Oil B.	Suspected oil.
Specific gravity . . .	0.921 ..	0.956
Optical rotation . . .	$\pm 0^\circ$ ..	$- 0^\circ 50'$
Refractive index . . .	1.4715 ..	1.4852

In the case of oils A and B no fraction had any odour suggestive of the presence of safrol.

In the case of the suspected oil, fraction No. 5 had an odour of safrol, though not very strong. But in the last fraction of the refractionated oil, a very distinct odour of safrol was present.

An attempt was made to identify the safrol, by oxidation with permanganate of potassium in acetic acid, in the hopes of obtaining homopiperonylic acid. An acid was obtained, but in too small amount for purification, so that no melting point determination could be made.

It was formerly considered that a pure French spike oil was always dextrorotatory, but the writer (E. J. P.) and Bennett showed that many samples are slightly lævorotatory up to  $- 3^\circ$ , and also yield a lævorotatory fraction on distilling the first 10 per cent. Birkenstock distinguishes the following groups of French spike lavender oils. Those produced in Ardiche, which are oils having a specific gravity 0.918 to 0.921; optical rotation,  $+ 7^\circ 48'$  to  $+ 9^\circ 36'$ ; optical rotation of the first 10 per cent. distilled,  $+ 8^\circ$  to  $+ 10^\circ$ ; ester content, 4 to 5 per cent.; and borneol content about 21 per cent. The Var produces oil rather more nearly approximating to the true lavender type, and having a specific gravity 0.9035 to 0.905; optical rotation,  $- 1^\circ 10'$  to  $0^\circ$ ; optical rotation of the first 10 per cent. distilled, about  $+ 2^\circ$ ; ester content, 2 to 3 per cent.; and borneol content, 20 to 32 per cent. Oils produced in Herault, Drôme, Gard, Basses-Alpes, and Alpes-Maritimes show characters intermediate between those of Ardiche and Var oils. This generalisation is in all probability due to accidental causes, and requires further investigation. At all events, pure French spike lavender oils should show the following characters :—

Specific gravity . . .	0.900–0.920
Optical rotation . . .	$- 2^\circ$ to $+ 7^\circ$
Refractive index . . .	1.4610–1.4680
Ester number . . .	3–22
Borneol . . .	30–37 per cent.

A little spike lavender oil is distilled in Dalmatia, but this does

not often come on to the market. Dalmatian spike lavender oil has a specific gravity about 0.902; optical rotation, up to  $-1^{\circ}$ , and contains about 30 per cent. of borneol.

Spike lavender oil contains as its principal constituent, the alcohol borneol, with some camphor, cineol, linalol, pinene, camphene and, possibly, terpineol. (Refer "La Lavande Française," Ch. Mourse, Paris, 1923.) For the influence of manures on lavender plants, refer Autran and Fondard (*La Parfumerie Moderne*, 1924, 49).

**LAVENDER WATER.**—This perfume is probably the most truly English perfumed toilet water in existence, although the lavender oil industry is essentially a French one, and large quantities of French lavender oil are used in its manufacture. Lavender water was originally manufactured by macerating the flowers in alcohol and then distilling the mixture. A small amount is so produced to-day, but only a trifling quantity. The bulk of the lavender water of commerce is manufactured by mixing the ingredients in the desired amount of alcohol and water, and allowing the mixture to mature. It should be remembered that English and French lavender oils are very different in odour, the former containing from 7 to 11 per cent. of linalyl acetate, and the latter up to well over 40 per cent. Hence lavender waters prepared from the two oils will differ very materially in odour. Some English makers use English oil only in its preparation, others use a blend of the two oils—which probably produces the finest result. In the manufacture, a fixative is necessary. Musk, civet, and a little concrete oil of orris are amongst the most useful. The ordinary text-books on practical perfumery provide numerous formulæ indicative of the composition of lavender water.

**LEBANON CEDAR OIL.**—The oil distilled from the wood of the Lebanon cedar, *Cedrus Libani*, is highly odorous. It has a specific gravity, 0.940 to 0.950; optical rotation,  $+66^{\circ}$  to  $+86^{\circ}$ ; and refractive index, 1.5120 to 1.5140.

**LEDUM PALUSTRE, OIL OF.**—This plant flourishes in northern America, where it is known as Labrador tea, and in Asia and parts of Europe. Its odour is sharp, but pleasant, and on distillation of the leaves and twigs about 1 to 2 per cent. of essential oil is obtained. It is generally so rich in stearophene that it is at ordinary temperature a solid mass. This, however, will depend on the exact stage of development of the plant when distilled, so that some specimens will remain liquid even at low

temperatures. The oil, which is also known as "wild rosemary," has the following characters :—

Specific gravity	.	.	.	0.920–0.960
Optical rotation	.	.	.	About + 4°
Refractive index	.	.	.	About 1.4850

The principal constituent of the oil is a sesquiterpene alcohol,  $C_{15}H_{26}O$ , known as ledum camphor. It forms long colourless needles, melting at 104°; of specific gravity at  $\frac{20^{\circ}}{4^{\circ}}$ , 0.9814; refractive index, 1.5072; boiling point, 281°; and specific rotation in alcoholic solution, + 8°. A ketone of the formula  $C_{15}H_{24}O$  is also present in the oil.

**LEMON OIL.**—This essential oil, which is of considerable value to the perfumer in the manufacture of certain types of perfume, such as eau de Cologne, is, for all practical purposes, obtained entirely from Sicily and Calabria. The tree itself, *Citrus limonum*, is a native of India which has been introduced into Europe and flourishes there, so that to-day it is cultivated on the Mediterranean littoral, in Sicily, Southern Italy, Spain and Portugal. Australia, Florida, California, and Jamaica also cultivate lemons on a commercial scale. The essential oil is not distilled, for the product is of such inferior quality as to be practically useless. It is obtained by "expression" or extraction from the peel of the fruit, by methods which will be found described under "Extraction of Perfumes."

From the commercial point of view, lemon oil presents very great difficulties in regard to quality. It is *par excellence* the oil which can usefully be manufactured in the terpeneless state. (See "Terpeneless Oils.") The result of this is that a huge quantity of terpenes are obtained as a by-product of the manufacture. The British Pharmacopœia has, for better or -worse, fixed a standard minimum figure for citral in lemon oil, namely, 4 per cent. The usual, almost inevitable, result of this type of standardisation has followed. There is not the slightest doubt that in many seasons the average citral value of the lemon oil produced in Sicily contains from 4.5 to 5 per cent. of citral. But it is equally certain that 90 per cent. of the oil reaching the consumer contains from 4.0 to 4.5 per cent. of citral, and a very large amount never contains more than 4 per cent. There can be no reasonable doubt that the majority of samples of lemon oil containing 4 to 4.2 per cent. of citral, and which are accepted as pure oil, are in

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fact high-grade pure lemon oils which have been deliberately reduced by the waste terpenes resulting from the manufacture of terpeneless lemon oil. From time to time samples of lemon oil have been examined in a given season which have been pressed in given districts, and limits laid down for the oils from the various districts. Such figures, however, should be taken with great reserve, as they are almost certainly only accidental, and no regular relationship exists between the characters of the essential oil and the district in which it is produced.

A pure Sicilian lemon oil has the following characters (with the reservation that most samples of the oil whose characters are close to the lower limit values are probably standardised down to such lower limits with terpenes, and so are not really pure samples) :—

Specific gravity	. . .	0.856–0.863
Optical rotation	. . .	+ 57° to + 64°
Refractive index	. . .	1.4745–1.4760
Non-volatile residue	. . .	2–4 per cent.
Citral	. . .	4–5.5 „

There are abnormal oils, which rarely come on to the market—for example, oils produced in Spain—whose characters differ from those of Sicilian oils both in regard to specific gravity, which may fall as low as 0.853, and citral value, which may be as low as 3 per cent.

E. J. Parry (*P. & E. O. R.*, 1924, 251) reports on an Australian lemon oil of undoubted purity which had the following characters :

Specific gravity	. . .	0.8558
Optical rotation	. . .	+ 62° 30'
Refractive index	. . .	1.4736
Citral	. . .	3.5 per cent.
Fixed residue	. . .	1.9 „

Australian oils do not appear to contain more than 3.5 to 4 per cent. of citral, but their flavour is excellent. The small quantity produced is entirely consumed locally.

Lemon oil contains as its principal odorous and flavouring constituent, the aldehyde citral. The bulk of the remainder of the oil is a mixture of *dextro*-limonene with a little *laevo*-limonene. There are also present, in small amount, the following bodies : octylene, possibly traces of pinene, camphene, phellandrene, methyl-heptenone, terpinene, octyl aldehyde, nonyl aldehyde, possibly citronellal, terpineol, linalyl acetate, geranyl acetate,

bisabolene, cadinene, citraptene, and possibly traces of methyl anthranilate.

Before discussing the methods used in the examination of lemon oil, the characters of terpeneless and sesquiterpeneless oils of lemon may be briefly outlined. As lemon oil is essentially an oil which contains only from 5 to 8 per cent. of true flavouring and odorous constituents, which are reasonably soluble in diluted alcohol, and about 90 per cent. of practically inodorous terpenes and sesquiterpenes which are very slightly soluble in alcohol, the concentration of the odorous and flavouring constituents by removal of the terpenes and sesquiterpenes effects an enormous saving of alcohol, and at the same time removes the non-odorous constituents, which are also very prone to oxidation and resinification, with a consequent detrimental effect on the odour of the oil. The terpenes are the lowest boiling constituents of the oil, and by removal of these only, a terpeneless oil results. But if the sesquiterpenes, which are the highest boiling constituents of the oil, are also removed, the resulting oil, freed from both terpenes and sesquiterpenes, is usually described as sesquiterpeneless. The two oils have the following characters (see E. J. Parry, *Chemist and Druggist*, 1913, 83, 378):—

	Terpeneless oils.	Sesquiterpeneless oils.
Specific gravity . . .	0.893–0.899	0.898–0.902
Optical rotation . . .	– 5° to – 8° 30'	+ 1° to – 3° 45'
Refractive index . . .	About 1.4810	—
Citral . . . . .	42–48 per cent.	65 per cent., or a little higher.

These limits must not be taken too rigidly, since Böcker has found specific gravities of 0.895 to 0.897, and optical rotations of – 5° 40' to – 7° 10' for sesquiterpeneless oils made by himself.

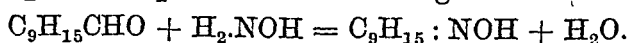
The trade in these concentrated oils is very large indeed, and the examination of the oils is of the highest importance. The degree of solubility in a particular strength of alcohol used by a given purchaser will, to an extent, enable him to decide upon the sample which best suits his purpose, provided it is pure. The real merit of the oil lies in its freedom, or comparative freedom, from hydrocarbons, and on its citral value. To determine the citral, the neutral sulphite method should be used (see “Aldehydes, Determination of”). This method cannot be used successfully

for ordinary lemon oil, which contains only about 5 per cent. of citral, but is fairly accurate in the case of the concentrated oils. To determine the amount of hydrocarbons in the so-called terpeneless and sesquiterpeneless oils, Böcker (*Jour. Prakt. Chem.*, 1914, ii., 89, 199) proceeds as follows. Five c.c. of the residue from the determination of the citral (made up, if necessary, from two determinations on 10 c.c. each) is introduced into a 600 to 700 c.c. separating funnel, into which 500 c.c. of 51 per cent. alcohol (by volume) cooled to ice temperature have been previously introduced. The mixture is well shaken, so that the remaining oxygenated constituents are dissolved in the alcohol. The separator is then inverted and allowed to stand upside down in a bath at ice temperature for eight to ten hours. It is then carefully re-inverted and allowed to stand until the alcoholic liquid is clear, when (often requiring two days) all but about 10 c.c. of the liquid is drawn off. Any oil drops adherent to the separator are washed down with ice-cold 51 per cent. alcohol, and the mixture again allowed to stand until quite clear. The alcoholic solution is then completely run off, and the hydrocarbons run off into a measuring cylinder and measured.

Böcker claims that a comparison of the residual hydrocarbons in a so-called terpeneless oil with the citral value enables one to decide whether citral from other sources has been added (*Jour. Prakt. Chem.*, 1914, ii., 90, 393). He states that any citral found above the following maxima indicates the presence, *pro tanto*, of added lemongrass citral.

Hydrocarbon content. Per cent.	Maximum of citral admissible. Per cent.	Hydrocarbon content. Per cent.	Maximum of citral admissible. Per cent.
0 . . .	66	30 . . .	46.2
5 . . .	62.7	35 . . .	42.9
10 . . .	59.4	40 . . .	39.6
15 . . .	56.1	45 . . .	36.3
20 . . .	52.8	50 . . .	33
25 . . .	49.5		

The determination of citral in ordinary lemon oil is practically invariably now carried out in the following manner, although numerous other methods have been suggested. It depends on the condensation of citral with hydroxylamine, which was first suggested by Walther (*Pharm. Zeit.*, 1899, 40, 621; 1900, 41, 585), and slightly modified by A. H. Bennett (*Analyst*, 1909, 34, 14). The process depends on the following reaction:—



It is carried out as follows: 20 c.c. of the lemon oil are mixed with 20 c.c. of 90 per cent. alcohol, 20 c.c. of a 5 per cent. solution of hydroxylamine hydrochloride in 80 per cent. alcohol, and 8 c.c. of approximately normal solution of caustic potash in alcohol. A blank experiment without the lemon oil is carried out simultaneously. The liquids are boiled briskly under reflux condensers for thirty to forty minutes, and then allowed to cool. When the contents of the flask are quite cold, the condensers are washed down with cold water in order to restore any traces of hydroxylamine to their respective flasks, and the flasks detached from the condensers. About 200 c.c. of cold water are then added to each flask, and a few drops of solution of phenolphthalein. The contents of the flasks are then neutralised to this indicator with seminormal alkali. The residual hydroxylamine is now titrated with seminormal sulphuric acid, using methyl-orange as indicator. A few drops of the indicator solution should be added to the flask in order to give a general indication of the approach of the end reaction, which should be determined by spotting on a white tile. Each cubic centimetre of seminormal acid in excess in the blank experiment is equivalent to 0.076 gram of citral.

Amongst the numerous other processes recommended for the determination of citral, the following may be referred to: E. J. Parry, *Chemist and Druggist*, 1900, 56, 376; E. M. Chace, *Jour. Amer. Chem. Soc.*, 28, 1472; R. S. Hiltner, *Jour. Ind. Eng. Chem.*, 1909, 1, 798; L. D. Little, *Jour. Amer. Pharm. Assoc.*, 1914, 3, 553; C. Kleber, *Schimmel's Bericht*, April, 1912, 64.

There has been much academic discussion as to the detection of turpentine as an adulterant of lemon oil. As a matter of fact, this adulterant is not to-day met with once in a thousand samples. If present, it is always in sufficient quantity to be readily detected by the optical rotation of the earliest fractions on distillation, in which the pinene becomes concentrated, with a consequent considerable reduction in the optical rotation. E. M. Chace (*Jour. Amer. Chem. Soc.*, 1908, 30, 1475) published an elaborate investigation on the detection of minute quantities of pinene in lemon oil by means of the microscopic identification of the nitrosochloride crystals obtained. He assumed that the identification of crystals of pinene nitrosochloride was decisive of the presence of added turpentine. It has, however, been definitely established that pinene is usually present in traces in pure lemon oil, so that Chace's method indicates nothing. Appreciable quantities of pinene which are detected by distillation methods may, of

course, be regarded as definitely indicating adulteration with turpentine.

**LEMONGRASS OIL.**—The lemongrass oil of commerce to-day is practically entirely East Indian in origin, the West Indian oil having for some years ceased to be produced at remunerative rates. The oil was up till recently described as being derived from *Andropogon citratus* and allied species, but a revision of the classification of the oils of the natural order *Gramineæ* by Stapf (*Kew Bulletin*, 1906, 8, 297) has practically settled the more correct nomenclature of these East Indian grasses, and it is clear that the parent plant of the lemongrass oils is *Cymbopogon flexuosus* (the old *Andropogon flexuosus* Nees), the Malabar or Cochin grass which is found freely in the Tinneveli district and in Travancore. Large areas in these districts have during the past ten years been planted with this grass. [According to the botanical researches of Stapf, the commercial lemongrass oil is obtained from two different plants. The oil produced on the Malabar coast is derived from *Cymbopogon flexuosus*, whilst *Cymbopogon citratus*, which only occurs in the cultivated state, yields an oil which differs in certain characters from the oil derived from the wild plants. *Cymbopogon citratus* is found in most tropical countries, especially in Ceylon, the Straits Settlements, Burma, Java, Mauritius, etc., and also in the Malay peninsula, where the lemongrass is cultivated on a comparatively large scale. According to Stapf, it appears that the lemongrass oil which is soluble in 70 per cent. alcohol is the product of *Cymbopogon flexuosus*, and the insoluble oil is derived from *Cymbopogon citratus*. The chemists of the Imperial Institute (*Bulletin*, June, 1914) put forward the view that the insolubility of much of the Cochin lemongrass oils was due to the fact that the oil was distilled by steam, so that the higher boiling and less soluble fractions are thus carried over, whilst (they say) the more soluble oils are distilled over a naked fire in the old-fashioned manner. There does not, however, appear to be any serious evidence to support this view, which is probably incorrect. There are two well-established facts, apart from any questions of botanical origin or methods of distillation, which must be taken into account in dealing with the solubility or insolubility of lemongrass oil. Firstly, it is well established that West Indian lemongrass oil was carefully examined before exportation, and found to be perfectly soluble in 70 per cent. alcohol. Yet when the consignments arrived in London, they were found to be insoluble in



70 per cent. alcohol. This appears to be due to the fact that the West Indian oil contains an olefinic sesquiterpene which rapidly oxidises, and so renders the oil insoluble. Secondly, it is clearly established that East Indian oils which, when examined before exportation, contain a given amount of citral, lose up to 3 or 4 per cent. of citral during the voyage to London, due to oxidation of the citral. It is, of course, impossible to say what the effects of this oxidation of the citral are, so that any deductions as to the question of the solubility of this oil must be taken with reserve.

A. W. K. de Jong has carried out a careful series of researches in order to determine the oil value of various portions of the plant in various stages of development, in order to determine the most profitable time for distillation. According to him, the leaves contain the highest percentage of oil, the latest formed leaves always containing more essential-oil than the earlier ones, in which the oil steadily diminishes. But whilst the actual quantity of the oil diminishes as the leaf becomes older, the citral value of the oil increases slightly. For example, the oil in the youngest leaves was found to contain 77 per cent. of citral, whilst that in the oldest leaves contained 83 per cent. A smaller amount of essential oil is also present in the leaf sheaths, and a small amount is also present in the larger bulbous roots. He concludes that the best time for cutting the grass for distillation is when four or five leaves have formed. Bacon (*Phil. Jour. Sc.*, 1909, 4, 111) states that a variety of grass which is probably *Cymbopogon citratus* is cultivated to a small extent in the Philippine Islands, and is found wild throughout the archipelago.

In the Tagal language the grass is known as *tanglad*, the name given to it by the Spanish Jesuit, Eusebius Nürnberg, who first described the plant. It is also known as *Paja de Meca*. The oil is also produced to some extent in Burmah, the Seychelles Islands, Uganda, and Bermuda. The characters of lemongrass oil (*i.e.*, the normal East Indian oil) are as follows :—

Specific gravity	.	.	.	0.895–0.907
Optical rotation	.	.	.	+ 1° to – 5°
Refractive index	.	.	.	1.4825–1.4885
Citral	.	.	.	70–85 per cent.

The oil is usually soluble, when freshly distilled, in 3 volumes of 70 per cent. alcohol, but, as mentioned above, loses its solubility on keeping, due to either oxidation or polymerisation of the hydrocarbon constituents. The following summary of the

characters of lemongrass oil from different parts of the world is from "The Chemistry of Essential Oils," vol. i., 4th ed., p. 73 :—

Origin.	Specific gravity.	Optical rotation.	Citral.
Ceylon . . . .	0.9058	— 0° 6'	Per cent. 76
India, Tyrna . . .	0.9021	— 0° 20'	72.5
„ Cochin . . . .	0.9053	— 0° 39'	84.5
„ Mariani . . . .	0.9140	— 0° 5'	73
Uganda . . . .	0.870–0.894	+ 0° 10' to — 0° 24'	64.5–75
Bermuda . . . .	0.8689	— 0° 2'	40
Montserrat . . . .	—	—	Over 74
New Guinea . . .	0.881–0.892	— 0° 11' to — 1° 15'	65–78
Mayotte . . . .	0.893	— 0° 23'	87
Seychelles . . . .	0.895–0.910	— 0° 15' to — 2° 40'	76–81
Formosa . . . .	0.865–0.914	0° to — 0° 8'	54–76
Celebes . . . .	0.880	— 0° 15'	69

Lemongrass oil contains as its principal constituent the aldehyde citral (*q.v.*), and is invariably sold on its citral value, the citral being usually determined by the bisulphite method unless otherwise specified. Traces of decyl aldehyde and citronellal are also present, as well as methyl-heptenone, geraniol, linalol, dipentene, and limonene. Stiehl (*Jour. Prakt. Chem.*, 1898, 57) claimed to have separated the aldehydic constituent into three distinct aldehydes, which he termed citral, allolemonal, and citriodor-aldehyde. This, however, has been shown to be incorrect by Döbner and other workers. Lemongrass oil is principally used for the separation of the citral for the manufacture of ionone. It is also used to a small extent on account of its verbena odour. Although often termed "verbena" oil, it must be distinguished from the true and more delicate verbena oil, which is derived from *Lippia citriodora*, one of the *Verbenaceæ*.

The roots of *Cymbopogon citratus* have been distilled and the oil examined at Buitenzorg (*Jaarb. dep. Land. in Ned-Indie, Batavia*, 1909, 64). The yield was about 0.2 per cent. of an oil of specific gravity about 0.947; optical rotation, — 1° 40' to — 3° 40'; and citral value, 11 per cent. (rhizomes) or 82 per cent. (bulbous roots).

**LENA-BATU GRASS.**—See "Citronella Oils" and "Grasses (Perfume) of India."

**LEPTOSPERMUM OILS.**—Although none of the oils of

this group are at present commercial articles, several of them have recently been the subject of scientific research in Australia, and deserve careful attention, as they are being examined as part of a systematic attempt to develop the perfume and other essential oils of the Empire in a manner which has not hitherto been attempted. These plants are members of the natural order *Myrtaceæ*. The first of the oils to be examined was that of *Leptospermum scoparium*, a plant known as *Manuka* by the natives of New Zealand. C. E. Atkinson found the essential oil to be a brown liquid of aromatic odour, having a specific gravity 0.914, optical rotation  $-17^{\circ}$ , and boiling between  $223^{\circ}$  and  $280^{\circ}$  (*Pharm. Jour.*, 1902, 69, 369).

The oil from *Leptospermum Liversidgei* is of extreme interest. It was first examined by Baker and Smith (*Jour. and Proc. Royal Soc. N.S.W.*, 1905, 39, 124), who stated that it contained citral (35 per cent.), geraniol, geranyl acetate, pinene, and a sesquiterpene. Its specific gravity was 0.8895; optical rotation,  $+9.2^{\circ}$ ; and refractive index, 1.4903 at  $16^{\circ}$ . Penfold (*ibid.*, 1922, 56, 82) has reopened the question, and found that very different results were obtained from plants which appear to be different forms—either two, or possibly three—of the shrub. He found these forms—possibly the result of environment, as, for example, is the case with lavender species—to yield essential oils as follows:—

(a) One yielding an oil to the extent of 0.25 to 0.3 per cent., as originally described, containing about 35 to 50 per cent. citral (no citronellal).

(b) A form yielding an oil, about 0.55 per cent., containing 70 to 80 per cent. citronellal (no citral).

(c) A form yielding about 0.6 to 0.8 per cent. of oil containing about 70 to 80 per cent. citral (no citronellal?).

As shown in the table on p. 415 of experimental results, material was obtained from Frazer Island, Queensland, which yielded essential oils in fair agreement with the composition of the oil as first described; whilst others collected at about the same time of the year, and in similar localities, yielded oils of different composition, as described above (see (b)).

As the material in each case was determined botanically to be the species *Liversidgei*, and as it is a shrub that is generally considered to be comparatively easy of recognition, the above mentioned conclusion is practically the only one that could be arrived at at the present time. The author would have preferred to have extended these observations over a further period of

years, supplementing the same with field inspections, but thought it advisable to record the results obtained to date in view of their possible economic influence, for the following reasons, viz. :—

(1) The distillation of the oil from *Leptospermum Liversidgei* (a) as originally described cannot be considered an economic proposition for the preparation of citral, in view of its low percentage yield (0.25 per cent.) and low content of aldehyde (only 35 to 46 per cent. This probably accounts for its neglect in the past.

(2) The type (c), yielding about three times as much oil as (a), of high citral content (70 to 75 per cent.), which would most probably be botanically diagnosed as (a) and thereby passed over, would most likely pay to distil. Good areas are available, particularly in certain of the northern river districts of New South Wales.

(3) The same remarks apply here as under (2). For an oil yielding citronellal to the extent of 82 per cent., free from other aldehydes, it is a noteworthy source of that constituent, especially on account of the ease of collection of the plant material. Provided sufficient material is available, it should be a serious competitor of the oil of *Eucalyptus citriodora*. In fact, the two oils are identical in odour and cannot be distinguished except by chemical examination.

The leaves and terminal branchlets of this species, cut in all instances as for commercial distillation, yielded the essential oils shown in the table on p. 415.

Penfold has also (*Jour. and Proc. Royal Soc. N.S.W.*, 1921, 55, 170) examined the oil from the leaves and terminal branchlets of the so-called "tea tree," *Leptospermum flavescens*, a tall graceful tree, about 4 to 12 feet high, growing extensively in the coastal and mountain districts within about 100 miles of Sydney, N.S.W. The following are the results of his investigations :—

Altogether 1,210 lb. of leaves and terminal branchlets, cut as for commercial distillation, were distilled, and gave an average percentage yield of 0.8 per cent., varying from 0.6 to 1.1 per cent., according to time of year.

The principal constituents of the oil so far determined are :—

(1) The dextrorotatory bicyclic sesquiterpene alcohol eudesmol, both solid and so-called liquid forms.

(2 and 3) A mixture of dextrorotatory sesquiterpenes, the one occurring in greatest quantity being considered identical with eudesmene, and the other aromadendrene.

(4)  $\beta$ -Pinene.

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Locality.	Percent- age yield of oil.	Specific gravity at 15° C.	Optical rotation.	Refractive index, 20° C.	Solubility in 70 per cent. alcohol.	Aldehyde content.		Remarks.
						Citral.	Citronellal.	
						Per cent.	Per cent.	
Broadwater, New South Wales	0.8	0.8960	+ 6.2°	1.4854	1 in 1.5 vol.	75	—	Type (c)
Forestry Depart., Brisbane	0.5	—	—	—	—	—	70	Type (b)
Frazer Island, Queensland	0.25	0.8885	+ 12.10°	1.4822	Insol. in 10 vols.	46	—	Type (a)
" "	0.33	0.8905	+ 12.75°	1.4820	"	46	—	"
Woodburn, New South Wales	0.55	0.8926	+ 11.2°	1.4603	1 in 1.5 vols.	—	82	Type (b)
Crescent Head, "	0.6	0.8910	+ 7.25°	1.4832	"	70	?	Type (c)
						(Aldehydes by bisul- phite method 74 per cent.)		

(5)  $\alpha$ -Pinene.

(6) A liquid phenol,  $C_{14}H_{20}O_4$ , giving an orange-red coloration with ferric chloride in alcoholic solution.

(7) Citral.

(8) Small amounts, not exceeding about 5 per cent., of unidentified alcoholic bodies.

Although the oil has never been distilled for commercial purposes, the writer considers it possesses certain economic possibilities, particularly in view of the large percentage of sesquiterpenes present in those samples where the solid eudesmol is practically absent. In its crude state it is of value for soap perfumery, and it could likewise be used as a substitute for cedarwood and similar oils. The sesquiterpenes themselves possess a fine cedarwood-like odour, and the author feels confident that in the near future these bodies will find suitable commercial application if obtainable in sufficient quantity.

The essential oil from *Leptospermum flavescens* var. *grandiflorum* (*Jour. and Proc. Royal Soc. N.S.W.*, 1920, 54, 197) differs entirely from the above, and has no economic interest. That of *Leptospermum odoratum* (*ibid.*), however, is of much greater interest. It is a yellowish oil with a pleasant terpene and rose-like odour. Three specimens of the oil had the following characters:—

	1	2	3
Yield . . . . .	0.88 per cent.	0.4 per cent.	0.9 per cent.
Specific gravity . . . . .	0.9246	0.9163	0.9280
Optical rotation . . . . .	— 16.32°	— 33.02°	— 19.02°
Refractive index . . . . .	1.4960	1.4989	1.4990
Ester number . . . . .	7.2	5.6	7.2
Ester number after acetylation . . . . .	91.9	57	87

The principal constituents of the oil are the following:—

(1) The dextrorotatory bicyclic sesquiterpene alcohol—eudesmol.

(2 and 3) A mixture of two levorotatory sesquiterpenes—eudesmene and aromadendrene.

(4)  $\beta$ -Pinene.

(5)  $\alpha$ -Pinene.

(6) Butyric and acetic acid esters of an unknown alcohol, as well as small amounts of an alcohol of citronellol odour (not geraniol nor

citronellol), also a small amount of both a solid and liquid phenol giving a bright red coloration with ferric chloride solution. Free acids, aldehydes, ketones, phellandrene, and limonene were not detected.

This oil is of considerable scientific interest, as it is the first in which the occurrence of the sesquiterpene eudesmene in nature has been noted, it having previously been obtained by dehydration of the corresponding sesquiterpene alcohol.

The presence of eudesmol in a leptospermum oil has not been noticed before, and its occurrence in quantity in such is not without interest. This sesquiterpene alcohol has only previously been recorded as being present in the oils obtained from the eucalypts.

Nopinene ( $\beta$ -pinene) has not previously been identified as a definite constituent of Australian essential oils. The oil of this leptospermum is therefore quite distinctive in character, and differs from that of any of its congeners so far described.

The alcohol of characteristic rose odour was only obtained in small quantity, but Penfold is of opinion that it is not geraniol nor citronellol.

Gardner (*Jour. Soc. Chem. Industry*, February, 1924) has examined the essential oil of *Leptospermum scoparium*, a shrub known in New Zealand as *Manuka*. The oil was distilled from the leaves and branchlets, which yielded 0.45 per cent. It had the following characters :—

Specific gravity . . . . .	0.921
Refractive index . . . . .	1.5000
Boiling range . . . . .	160°–270°

Its composition is as follows :—

	Per cent.
Phenols (leptospermol) . . . . .	2.8
Terpenes . . . . .	2.8
Esters of cinnamic acid . . . . .	4.8
Other esters (including those of an unidentified alcohol of rose odour) . . . . .	12.9
Non-volatile matters . . . . .	7.7
Sesquiterpenes . . . . .	69

*Leptospermum citratum* is described by Penfold (*Bulletin* No. 5, 1923, Technological Museum, Sydney) as a valuable oil-yielding plant worthy of attention.

This interesting tea tree, the essential oil of which was first described by Penfold in conjunction with Messrs. Challinor and

## P E R F U M E R Y

Cheel during 1918, grows somewhat sparsely in parts of the northern rivers district of New South Wales, and Springbrook and Palmwood of Queensland. The essential oil, which is usually of a pale yellow colour, possesses a strong pleasant lemon odour suggestive of its principal constituents, citral and citronellal, which are present to the extent of not less than 90 per cent.

Its chemical and physical constants as then published were :—

Yield . . . . .	1.73–1.85 per cent.
Specific gravity $15^{\circ}$ . . . . .	0.8841
Optical rotation . . . . .	+ 3.6°
Refractive index, $20^{\circ}$ . . . . .	1.4730
Solubility in 70 per cent. alcohol . . . . .	1 in 2 vols.
Aldehyde content . . . . .	90 per cent.

Four samples from cultivated plants were examined, with the following results :—

### *Plants cut on*

	March, 1919.	9th Nov., 1920.	10th Nov., 1921.	24th Oct., 1922.
Colour of oil . . . . .	Pale lemon tint.	Pale lemon tint.	Pale lemon tint.	Pale lemon tint.
Yield of oil (fresh material) . . . . .	0.8 per cent.	1.46 per cent.	1.1 per cent.	1 per cent.
Specific gravity $15^{\circ}$ . . . . .	0.8814	0.8811	0.8794	0.8833
Optical rotation . . . . .	+ 5°	+ 4°	+ 4.55°	+ 3.95°
Refractive index $20^{\circ}$ . . . . .	1.4695	1.4708	1.4692	1.4701
Solubility in 70 per cent. alcohol . . . . .	—	—	1 in 1.3 vol.	1 in 1.2 vol.
Aldehyde content (bisulphite method) . . . . .	95 per cent.	95 per cent.	95 per cent.	95 per cent.

The aldehydes consist approximately of equal parts of citronellal and citral, but vary slightly during the seasons. The optical rotation is a useful guide as to the respective quantities of each aldehyde present, as the citronellal possesses an optical rotation of + 10° at  $20^{\circ}$ . It is possible by direct fractional steam distillation of the leaves to obtain about 70 per cent. of the oil, containing about 99 per cent. of aldehyde.

**LIATRIS ODORATISSIMA.**—This plant is found to a con-



siderable extent in the savannahs of North Carolina, where it is known as "hound's tongue" or "vanilla plant." It contains an appreciable amount of coumarin, and the dried leaves are used for perfuming cigars. The leaves also contain a body known as liatrol, having a persistent and not very pleasant odour. *Liatris spicata* is an allied plant which yields a small quantity of an essential oil containing coumarin (W. F. Henry, *American Jour. Pharm.*, 1892, 64, 603).

**LIBOCEDRUS DECURRENS.**—This tree is known in the United States as the incense pine. Schorger (*Jour. Ind. Eng. Chem.*, 8, 22) has examined the essential oil distilled from the needles and branches, and also that from the bark. From the needles and branches he obtained from 0.18 to 0.3 per cent. of an oil having a colour varying from light-green yellow to dark-brown green. The oil, obtained by distilling the bark, is feebly coloured light-green yellow. The following, in tabular form, are the author's principal results :—

	Oil from needles and branches.	Oil from bark.
Specific gravity at 15° . . . . .	0.8655–0.8766	0.8621
Optical rotation . . . . .	– 3.20° to + 36.68°	+ 1.10°
Refractive index . . . . .	1.4754–1.4778	1.4716
Acid value . . . . .	0.48–1.30	0.60
Saponification value . . . . .	18.49–27.82	3.20
"    after acetylation . . . . .	28.64–46.24	9.53
<i>l</i> - $\alpha$ -Pinene . . . . .	12–16 per cent.	75–85 per cent.
<i>d</i> -Sylvestrene . . . . .	54–58    ,,	5–6       ,,
<i>d</i> -Limonene . . . . .		
Dipentene . . . . .		
Bornyl acetate . . . . .		

Schorger has also identified a sesquiterpene, libocedrene, having the following characters :—

Boiling point . . . . .	260°–280°
Specific gravity at 20° . . . . .	0.9292
Optical rotation . . . . .	+ 6.4°
Refractive index . . . . .	1.4994

**LICARI OIL.**—See "Bois de Rose."

**LICHENOL.**—This body was isolated from the extract of the lichen *Evernia Prunastri*, which is the principal lichen used for the preparation of "Mousse de Chêne" (*q.v.*).

It has been critically examined by St. Pfau (*Les Parfums de France*, May, 1924, 137; *Berichte*, 57, 468); and by Späth and Jeschki (*Berichte*, 57, 471).

The opinion that this body is a phenol-ketone related to cetrarine is shown to be incorrect. St. Pfau finds it to melt at  $73.5^{\circ}$  to  $74^{\circ}$ , and to possess a powerful odour of mousse de chêne, which is in agreement with the observations of its discoverer, Gattefossé. He finds its formula to be  $C_{11}H_{14}O_4$ . Chemically, it is ethyl evernate, and he has prepared it synthetically by the action of ethyl alcohol on evernic acid. The corresponding methyl ether appears to be identical with sparassol, which is formed by the fermentation of sugar solutions by pure cultures of *Sparassus ramosa*. Späth and Jeschki have synthesised evernic acid by the interaction of orcinic acid and diazomethane.

**LILAC.**—The perfume sold under this name is not a natural perfume at all. The oil is not extracted, and its constituents are not completely known. Its general composition is similar to that of lily of the valley, but terpineol is the dominating constituent. Hydroxycitronellal is also of great use in this perfume. Artificial substances sold under the name syringol or artificial lilac are based on these substances. The ordinary lilac is *Syringa vulgaris*, but many other species or varieties of the plant have a fine odour. Guerbet (*Comptes Rendus*, 146, 1405) has prepared synthetically methylbenzyl-ethyl alcohol (boiling point,  $244^{\circ}$  to  $246^{\circ}$ ), and ethylbenzyl-ethyl alcohol (boiling point,  $258^{\circ}$  to  $261^{\circ}$ ), both possessing lilac odours.

**LIMENE.**—This name was originally given to the sesquiterpene which was isolated from oil of limes by Burgess. It has been found in various other essential oils, and was identified as being the same body as bisabolene, isolated from bisabol myrrh by Tucholka (*Arch. d. Pharm.*, 1897, 235, 292).

**LIMES, OIL OF.**—This oil is used on a considerable scale for flavouring purposes, and to a small extent in perfumery, as its odour is found of great value in certain types of eau de Cologne, etc. The ordinary oil of limes of commerce is that produced in the West Indies from the fruits of *Citrus medica* var. *acida*. It is cultivated more particularly in the islands of Montserrat, Dominica, Trinidad, Antigua, Barbados, St. Lucia, and Martinique. Two types of the West Indian oil exist. That found in larger quantity is the distilled oil obtained as a by-product in the evaporation of lime juice. It has a sharp odour, quite charac-

teristic and pleasant, but not recalling that of citral. It is a colourless liquid of specific gravity 0·859 to 0·872; optical rotation,  $+ 33^{\circ}$  to  $+ 48^{\circ}$ ; refractive index, 1·4700 to 1·4750; and contains from 1 to 2 per cent. of citral. The hand-pressed oil, obtained by an *ecuelle* process, is of far more value, and of finer odour. It is of a golden yellow colour, and has an intense odour recalling that of exquisitely fine lemons. It has a specific gravity 0·878 to 0·901; optical rotation,  $+ 30^{\circ}$  to  $+ 38^{\circ}$ ; refractive index, 1·4820 to 1·4860; and contains from 6 to 9 per cent. of citral. On evaporation it leaves a residue (at  $100^{\circ}$ ) of about 10 to 18 per cent., which has a saponification value from 160 to 181. The oil contains citral, bisabolene, citroptene, and possibly methyl anthranilate.

Italian lime, or limette, oil is expressed from the peel of the fruits of *Citrus limetta*. In Calabria this tree is known as *Arancio* or *Limoncello di Spagna*. These lime trees were cultivated to a considerable extent, and were used for grafting the bergamot upon. But as their roots are very liable to the so-called gum disease, the bergamot is now usually grafted on the bitter orange tree. Only a small amount of Italian oil of limes appears in commerce. It is a brownish yellow oil of excellent odour, having a specific gravity about 0·872; optical rotation,  $+ 58^{\circ}$ ; and saponification value, 75. It contains limonene, linalol, and linalyl acetate (up to 26 per cent.).

Terpeneless oil of limes is a regular commercial article, and of course, like terpeneless oil of lemon, possesses the advantages of greater odour value and higher solubility. The terpeneless and sesquiterpeneless oils have the following approximate characters:—

	Terpeneless.		Sesquiterpeneless.	
	Distilled.	Expressed.	Distilled.	Expressed.
Specific gravity	0·903	0·896–0·905	0·900	0·923
Optical rotation	$+ 5^{\circ}$	$+ 2^{\circ}$ to $- 2^{\circ}$	$- 2^{\circ}$	$- 5^{\circ}$
Refractive index	1·4830	1·4860	1·4880	1·4840

The leaves of the West Indian lime tree yield an oil having an odour resembling that of the oil expressed from the fruits. It has a specific gravity 0·878; optical rotation,  $+ 37^{\circ}$ ; and ester value, 23. It contains about 43 per cent. of citral.

E. J. Parry (*Chemist and Druggist*, 1900, 56, 993) examined the oil distilled from the flowers of the Italian lime tree, and found it to have a specific gravity 0.870, and optical rotation  $+ 21^{\circ} 30'$ . It contains linalol and methyl anthranilate.

**LILY PERFUME.**—The perfume of the lily, in commerce, is practically restricted to that of lily of the valley. The only natural perfume available is the concrete or absolute, no essential oil ever being distilled. The perfume as sold is usually based on a certain amount of this natural product, together with synthetics, of which terpineol, linalol, and hydroxycitronellal are the principal. These are fortified with such natural perfumes as jasmine, traces of benzaldehyde, and other substances according to individual taste. The perfume is also known as "Muguet." According to J. Gattefossé (*La Parfumerie Moderne*, through *P. & E. O. R.*, 1917, 271), the French industry of growing the blossoms for the market is an important one. The French call the lily the "*Muguet du Mai*"—in central France the first flowers appear at the beginning of May; many other plants, such as the Solomon's seal, and even hyacinths, share also in the style "*Muguet*," but the lily of the valley is "*muguet*" *par excellence*, and the writer urges that it alone should bear the name. The cultivation is addressed to securing the choice flower heads at Christmas and the New Year. For this purpose it is necessary to force them. Before the war the main supply of forced lilies came from Germany, where the industry has been established since 1848, largely in the neighbourhood of Berlin, Hamburg, and especially Erfurt. Since 1890 the cultivation has so progressed in France that it promises to become permanent and remunerative. Up to the present, however, French production has had little left over available for export, the home demand, particularly for Christmas festivities, being enormous. The first step in growing lilies for the market is to obtain a supply of wild rhizomes bearing latent flower buds called turions. These are planted in the autumn in a well dug, properly prepared earth; after earthing up they are well watered and manured, and during growth constant dressing and watering is necessary. It usually takes three years for the plants thus cultivated to be ready for forcing, but by careful selection and preparation it is possible to obtain rhizomes sufficiently strong to force in a year. As a general rule the plants are kept in a cool greenhouse, and taken as required into the forcing house, which, commencing at a temperature of  $20^{\circ}$ , is in the second week raised to  $25^{\circ}$  to  $30^{\circ}$ . The clumps are covered with moss or sawdust.

They must be very frequently watered. Towards the end of the third week in the forcing house the flower stalks appear, and when the florets begin to open they are taken into a cooler house, and two days after are transferred to the open air. The forced roots are exhausted, and do not produce new shoots. It is the general custom to draw the rhizomes for forcing from the wild plants, but attention is being paid to a cultivated variety bearing larger florets and commanding a higher price.

**LINALOE OIL.**—Commercial linaloe oil must not be confused with so-called “Cayenne linaloe” oil or oil of “Bois de Rose.” True or Mexican linaloe oil is the product of the distillation of the wood of several species of *Bursera*, and to some extent, possibly, from the fruit. The species which are principally employed for the distillation of the oil are *Bursera Delpechiana* and *Bursera Aloexylon*. In 1904 Dr. Altamirano (*Report of the Inst. Med. Nac. Mexico*, 1904, January–March) made an exhaustive report on the question of the production of linaloe wood and its oil. He stated that it is obtained principally from the districts of Oaxaca, Puebla, Guerro, Morelos, and Michoacan, as far down as Colima. The natives distinguish three kinds of the wood: fine, common, and caraway linaloe. The first has an exceedingly fine odour, the second a less fine odour, and the third distinctly recalls the odour of caraway. They distinguish the “linaloe” tree from the “copal limon,” whose wood is said to be more spongy, and which yields most of the linaloe oil of commerce. It is a very hardy tree, requiring but little attention, and flourishes on even very rocky soil. It can readily be propagated by cuttings, but very few attempts have been made in this direction, although the tree will not yield any oil until it is about twenty years old. It is probable that much of the commercial oil found on the market during recent years has been distilled from a mixture of the wood and fruits. The fruits ripen in September, as greenish to red berries, about the size of peas. They yield about 3 per cent. of oil, which is higher than that obtained from even the best varieties of wood. Distillation commences in July and continues until well in September. The fruit oil has not the sweet odour of the wood oil, and has a tendency to resinify, so that it is almost invariably mixed with the wood oil before exportation. If the berries are placed in boxes and covered with bags and kept at a slightly elevated temperature for three or four days, they ferment and yield a higher percentage of oil. The finest oil is yielded by wood cut from trees which are from forty to sixty years old. In

the case of young trees, the oil yield is sometimes artificially increased by notching the stems, which induces a pathological secretion. This wounding is effected by removing strips of the bark about 40 cm. long, 20 cm. wide, and 5 cm. deep, either parallel to the axis of the stem or, preferably, diagonally thereto. If this reveals that the tree possesses heart wood yellow coloured and aromatic, it can be used at once for distillation purposes, but if not, it is allowed to stand for a year or two till it has "acquired a heart." The cut is so made that the rain water flowing down the tree shall not pass over the wound. If, however, in spite of this the rain should cause the wood to commence to rot, the injured wood is planed off, so as to stop the decay. The Indians were induced to adopt this practice by their observations that linaloe tree roots often contained so much essential oil that it could be expressed by the fingers, and that trees which had lost their branches through wind storms produced a great deal of essential oil. This wounding of the trees, which converts trees poor in oil into rich oil trees, is usually performed in April and in September, the latter being the more effective. Distillation is conducted from early in January, or even late in December, until June. The smaller distillers are often more or less uncivilised Indians who do not even speak Spanish, and no real factories can be said to exist. The conditions of life in the linaloe districts are exceedingly difficult, so that distillation is, of necessity, of a very primitive character. The yield of oil is, as above mentioned, up to 3 per cent. on the fruits, but is rarely above 2.5 per cent. on the wood. According to *Schimmel & Co.*, who sent a representative to visit a distillery at Chiantla, Puebla, the stills used are of a very primitive character. With the exception of the copper helmet, all parts of the still are made of galvanized iron. The still is heated by direct fire, and has a height of about 5 feet, and a diameter of about 4 feet. The lower part is provided with a piece of iron pipe, which is closed with a plug made of wood, around which banana leaves are wrapped. Through it the water is drained off at the completion of distillation. The helmet, which is provided with a condenser, is connected with a barrel condenser by means of the necessary pipes. The stills (according to *Schimmel & Co.*) are usually erected near a mountain stream, and frequently very remote from the place where the distillation material is produced, apparently on account of the absolute necessity of a plentiful supply of water for the distillation. The capacity of the still is usually about 250 kilos of the chipped wood, with which it is

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filled to within about 10 inches of the top. Water is added to cover the wood, and the still is then heated by means of a naked fire. When the oil is, on rare occasions, distilled in Europe, a yield of 7 to 9 per cent. of essential oil has been obtained. Whether this is due to improved methods of distillation, to fermentation of the wood, or to accidental circumstances, it is impossible to say.

The earliest investigation of the oil was by Verneuil and Poisson, but the conclusions at which they arrived are not of any weight to-day. Semmler (*Berichte*, 1891, 207) was the first to isolate the true odorous constituent of the oil, which he termed linalol, which has been described under various names, such as licareol or coriandrol, in a more or less impure condition. It also contains the alcohols geraniol and *dextro*-terpineol and, according to Schimmel & Co. (*Report*, November, 1908, 84), methyl-heptenol. Traces of linalol oxide, sesquiterpenes, octylene, nonylene, and an olefinic terpene (probably myrcene) are also present. The alcohol linalol is by far the most important constituent, being present to the extent of about 90 per cent.

Linaloe oil is a colourless or pale yellow oil of characteristic sweet odour, that of linalol predominating. Its characters usually fall within the following limits :—

Specific gravity	. . .	0.875–0.898
Optical rotation	. . .	— 3° to — 15° (but sometimes dextrorotatory)
Refractive index	. . .	1.4590–1.4655
Acid value	. . .	0–6
Ester	. . .	5–20 (rarely higher)

It is soluble in 3 volumes of 70 per cent. alcohol. It must be remembered, however, that methods of distillation vary so much that oils are to be found with characters outside these limits. For example, oils high in linalol oxide will sometimes have a specific gravity over 0.900. According to Roure-Bertrand *Fils* (*Bulletin*, October, 1907, 16; October, 1908, 18), the *dextro*-rotatory oils which are sometimes found in commerce are either the oil distilled from the seed or are mixtures of wood oil with seed oil. Such oils may have an ester value up to 40.

The principal constituent of linaloe oil is linalol, but, as this alcohol is very easily dehydrated, it is impossible to determine its amount by the ordinary acetylation method, so that special precautions are necessary. (See under "Alcohols, Determination of.") The fractional distillation of this oil gives exceedingly useful

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results and enables most adulterants to be detected. Four oils were examined by E. J. Parry and C. T. Bennett which had the following characters :—

	1.	2.	3.	4.
Specific gravity . . .	0.882	0.882	0.877	0.879
Optical rotation . . .	— 11°	— 10°	— 11° 30'	— 12° 10'

On separation into fractions these oils gave the following results :—

	I.		II.	
	Specific gravity.	Rotation.	Specific gravity.	Rotation.
10 per cent. . . .	0.868	— 11°	0.870	— 10° 30'
20    "    . . . .	0.870	— 11° 30'	0.870	— 10° 20'
20    "    . . . .	0.871	— 13°	0.871	— 10° 40'
20    "    . . . .	0.872	— 13°	0.873	— 10° 10'
20    "    . . . .	0.876	— 12°	0.877	— 9° 40'
10    "    residue .	0.913	—	0.909	—

	III.		IV.	
	Specific gravity.	Rotation.	Specific gravity.	Rotation.
10 per cent. . . .	0.872	— 11° 40'	0.871	— 12°
20    "    . . . .	0.871	— 11° 30'	0.871	— 13°
20    "    . . . .	0.873	— 12°	0.873	— 13° 20'
20    "    . . . .	0.874	— 11° 50'	0.874	— 11° 50'
20    "    . . . .	0.876	— 11° 10'	0.876	— 10° 30'
10    "    residue .	0.909	—	0.912	—

Linaloe oil has been from time to time found adulterated with fatty oils, but the decreased solubility, increased specific gravity, and high ester value indicate this adulterant at once. Shiu oil (*q.v.*) has been recommended as a substitute for linaloe oil, which



it much resembles. As an adulterant, it is exceedingly difficult to detect. But as shiu oil contains camphor, the detection of this ketone is practically conclusive evidence of the presence of this oil as an adulterant. The best method for the determination of camphor in the oil is as follows. Fifty grams of potassium permanganate and 300 c.c. of water are placed in a 2-litre flask and cooled with ice. Ten grams of linaloe oil are added slowly, drop by drop, so that the addition takes about half an hour. The oil rapidly oxidises to a soluble product, and the camphor can be steam distilled unchanged. The distillate is saturated with salt, and the camphor extracted with ether, which is evaporated at a low temperature and the camphor weighed.

Camphor can also be detected by conversion into its semicarbazone. The oil is steam distilled so as to get rid of any fixed residue. Twenty-five cubic centimetres of the oil so distilled are treated with 1 gram of semicarbazide hydrochloride, 1 gram of sodium acetate, and 25 c.c. of 90 per cent. alcohol. After being allowed to stand for twenty-four hours, 1 gram of sodium bicarbonate is added, and the whole is steam distilled. The distillation residue is heated on the water bath, and then cooled. The semicarbazone of camphor separates if camphor be present. On recrystallisation from alcohol this is obtained in a fair state of purity, but not sufficiently so for a melting point determination. But on warming with dilute sulphuric acid the odour of camphor at once becomes apparent.

J. C. Umney (*P. & E. O. R.*, 1916, 62) has described two samples of oil having a very high ester value. It is possible that these were derived from other species of *bursera*, and their odour recalled those of lavender and petitgrain rather than that of normal linaloe oil. These oils had the following characters :—

	1.	2.
Specific gravity . . . .	0.897	0.893
Optical rotation . . . .	— 2° 30'	— 2° 30'
Refractive index . . . .	1.4600	1.4610
Esters . . . . .	52.4 per cent.	48.7 per cent.
Total linalol . . . . .	54.8 „	57.6 „

The pure seed oil has been examined by *Roure-Bertrand Fils*

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(*Bulletin*, October, 1907, 16 ; October, 1908, 15), and stated to have the following characters :—

Specific gravity	0.8858–0.8883
Optical rotation	+ 1° 30' to + 8°
Refractive index	1.4655 at 18°
Esters	10.8 per cent.

It contains methyl-heptenone, linalol, geraniol, nerol, and terpineol.

**LINALOL.**—This substance is an open chain alcohol, of the formula  $C_{10}H_{18}O$ , which is found in the free state to a considerable extent in the essential oils of linaloe and “bois de rose.” In the form of esters, it is found as the predominating constituent of oils of bergamot and lavender. It is isomeric with geraniol and nerol. It is, both in the free state and in the form of various esters, of the greatest value to the perfumer. It has been isolated from various essential oils in a more or less impure condition, and numerous names have been assigned to it. For example, coriandrol, licareol, and lavendol have all been found to be merely impure linalol. Linalol is not an easy substance to purify, as it yields practically no crystalline compounds. The purest specimens that have been prepared have been found to have the following characters :—

	From			
	Lavender oil.	Bergamot oil.	Linaloe oil.	Lime oil.
Boiling point	198°	198°	198.5°	198.5°
Specific gravity	0.8725	0.872	0.877	0.870
Refractive index	1.4640	1.4629	1.4630	1.4668
Optical rotation.	— 10° 35'	— 16°	— 2°	— 17° 37'

Specimens have, however, been prepared with optical rotations about  $\pm 20^\circ$  from orange and lime oils, so that this probably represents the true optical rotation.

According to Tiemann (*Berichte*, 29, 201 ; 31, 837), a pure linalol may be prepared by heating the fraction of linaloe oil rich in linalol with metallic sodium, under reduced pressure, until no more sodium is dissolved. When the mixture is cold, the liquid is decanted from unchanged sodium and mixed with ether and phthalic anhydride. After being allowed to stand for several

days, the mixture is shaken with water, which dissolves the linalyl-sodium phthalate, the unchanged linalol and terpenes remaining dissolved in the ether. The resulting linalyl phthalate is hydrolysed by alcoholic potash and the pure linalol is extracted with ether.

Linalol yields citral on oxidation, and is also converted into geraniol by boiling for two hours with acetic anhydride and saponifying the resulting ester. It yields a phenylurethane melting at  $65^{\circ}$ , and a naphthylurethane melting at  $53^{\circ}$ . Linalol is used to a considerable extent for manufacturing the various esters of linalol which are used in perfumery.

**LINALYL ACETATE.**—Linalyl acetate,  $C_{10}H_{17}.OOC.CH_3$ , is the ester to which oil of bergamot almost entirely owes its odour. Lavender oil is also an oil containing a high percentage of this ester, and it also occurs in petitgrain, ylang-ylang, neroli, jasmine, and gardenia oils in sufficient amount to influence their odours. It is prepared artificially to a considerable extent by acetylating linalol obtained from linaloe oil, but the acetylation is always incomplete, so that a pure ester cannot be obtained. It is a colourless oil having a powerful bergamot odour, and having approximately the following characters (*i.e.*, for good-quality commercial specimens) :—

Specific gravity	.	.	.	0.900–0.910
Refractive index	.	.	.	1.4500–1.4550
Actual esters	.	.	.	88–95 per cent.

It is used in the preparation of most artificial perfumes of the jasmine, ylang-ylang, and tuberose types. The absolutely pure ester, which has been prepared by Tiemann by the interaction of linalol sodium and acetic anhydride, boils at  $115^{\circ}$  to  $116^{\circ}$  at 25 mm., or at about  $220^{\circ}$  at atmospheric pressure. Its specific gravity is 0.913, and optical rotation from  $+6^{\circ}$  to  $-6^{\circ}$ .

**LINALYL BUTYRATE.**—This useful ester of linalol has the formula  $C_{10}H_{17}.OOC.C_3H_7$ . It is prepared by the esterification of linalol and butyric acid and, like the acetic ester, is never absolutely pure. It resembles geranyl butyrate in odour, and is used to impart a fruity odour to floral perfumes.

**LINALYL FORMATE.**—This ester,  $C_{10}H_{17}.OOCH$ , is prepared in the same way as the acetic ester, and, like it, is never fully esterified. It is an oil of distinctive odour, somewhat resembling that of the acetate, and boiling at  $189^{\circ}$  to  $192^{\circ}$ .

**LINALYL PROPIONATE.**—This ester,  $C_{10}H_{17}.OOC.C_2H_5$ ,

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is prepared in the same manner as the acetate, and has a sweet bergamot-like odour recalling that of lily of the valley. It boils at 115° at 10 mm. pressure.

**LINDEN PERFUME.**—The linden tree, *Tilia Europea*, is a favourite ornamental tree belonging to the natural order *Tiliaceæ*, and is found in southern Europe and northern Asia. Its flowers are very fragrant. A small amount of essential oil has been obtained from its flowers (about 0.038 per cent.). Its only identified constituent is farnesol,  $C_{15}H_{24}O$  (Winckler, *Pharm. Zentral*, 1837, 781). Perfumes of this name are almost invariably artificial.

**LINDERA PRÆCOX, OIL OF.**—Shinozaki (*Jour. Chem. Ind. Japan*, through *Jour. Soc. Chem. Ind.*, 1921, 24, 444) has examined the essential oil of this plant, which is known in Japan as *Aburachan*, and finds it to have the following characters:—

Specific gravity . . . . .	0.9094–0.9178
Refractive index . . . . .	1.4850–1.4866
Optical rotation . . . . .	— 3° 57' to — 5° 1'
Acid value . . . . .	0.7–0.9
Saponification value . . . . .	45.7–48.7
Saponification value after acetylation . . . . .	90.5–98.6

The oil contains  $\alpha$ -pinene, camphene, cineol, an aliphatic terpene, borneol, geraniol, esters of borneol and geraniol, caryophyllene, cadinene, a sesquiterpene alcohol, and a tertiary alcohol not identified. The acids combined in the form of esters included acetic, decylenic, and probably citronellie.

**LIPPIA OILS.**—The essential oil of *Lippia citriodora* is the true verbena oil or vervain oil (*q.v.*). There are, however, other species of highly aromatic odour. Amongst these is *Lippia urticoides*, a native of Brazil, whose fragrant flowers yield, according to Peckolt (*Ber. d. deutsch. pharm. Ges.*, 1904, 14, 469), 0.063 per cent. of essential oil having an odour resembling that of neroli. It has a specific gravity 0.908 at 23°, and a blue fluorescence, probably due to the presence of methyl anthranilate. *Lippia scaberrima* is a plant found in South Africa, where it is commonly known as *Beukers boss*. Power and Tutin (*Amer. Jour. Pharm.*, 1907, 79, 449) obtained 0.25 per cent. of essential oil from the dry plant. It was yellowish brown in colour, with an odour recalling those of lavender and sage. Its specific gravity was 0.950; optical rotation, + 7° 36'; and boiling range, 220° to 230°. Its constituents have not been determined.

**LITSEA OILS.**—The leaves of *Litsea odorifera*, a plant known in Java as *Trawas*, yield an odorous essential oil which has been examined by Romburgh (*Kon. Akad. Wet. Amsterdam*, 1911, 325). He found the oil to contain nonylene-methyl-ketone, methyl-nonyl-carbinol, and undecenol. Its specific gravity varied from 0.836 to 0.846, and its optical rotation from  $-0^{\circ} 10'$  to  $-7^{\circ}$ . Gardies (*La Parfumerie Moderne*, 1923, 107) has examined the essential oil which is sold in Tonkin under the name *Maychang*. This appears to be the distillate from the flowering tops of *Litsea citrata*. The highly odorous flowers of this tree, which grows to 30 feet or more in height, are used for perfuming tea. The oil has a sweet odour recalling linalol, and appears to contain geraniol, linalol, citral, and limonene. The characters of the oil were found to be as follows:—

Specific gravity at $20^{\circ}$	. . .	0.866
Optical rotation	. . .	$+ 20^{\circ} 2'$
Refractive index	. . .	1.4620
Esters	. . .	2.67 per cent.
Free alcohols	. . .	44.9   ,,
Citral	. . .	8.15   ,,

This plant is possibly identical with *Tetranthera citrata* of northern India, Java, and the Indian archipelago. The fruit of this plant yields 4 to 5 per cent. of oil of specific gravity 0.885 to 0.898; optical rotation,  $+ 6^{\circ}$  to  $+ 13^{\circ}$ ; and aldehyde content, 79 to 86 per cent. The principal constituent is citral, with some geraniol, geranyl esters, and a terpene. The leaves yield an oil containing cineol, citral, and probably geraniol; the bark oil contains citral, citronellal, geraniol, and geranyl esters. If these plants are identical, it is clear that the oils are very different according to the place in which the tree grows. The oil from the bark contains citral, citronellal, and a large amount of an alcohol (geraniol?). (See *Roure-Bertrand Fils, Bulletin*, November, 1907, 18.)

**LONICERA PERFUMES.**—See “Honeysuckle.”

**LOTUS PERFUMES.**—The so-called lotus perfumes are entirely artificial, no perfume being extracted from any plant which could be associated with the lotus of the ancients. It is possible that *Nelumbium speciosum* is the sacred lotus of the Egyptians, who appear to have regarded it with great reverence, especially in their worship of Isis. It has been regarded as sacred also by many Oriental races, and figures, largely as a religious emblem, on much Chinese porcelain. The so-called lotus perfume

to-day is any heavy "Oriental" odour compounded, according to the taste of the individual, from such natural perfumes as patchouli, benzoin, storax, etc., with the assistance of artificial perfumes such as phenyl-ethyl alcohol, cinnamic alcohol, and similar bodies.

**LOPHANTHUS OILS.**—There are several species of *Lophanthus* (N.O. *Labiatae*) which yield odorous essential oils. Of these *Lophanthus rugosus* is the principal. It is found in the wild condition in northern America and in eastern Asia. Vilmorin and Levallois (*Bull. Soc. Chim.*, 1914, 342) have examined the oil, which is an amber-coloured liquid having an odour recalling that of aniseed, of specific gravity 0.962 to 0.967; optical rotation,  $+5^{\circ}$  to  $+6^{\circ}$ ; and ester value, 3.7. It contains as its principal constituent methyl-chavicol, and also some limonene. The plant *Lophanthus anisatus* yields a small amount of essential oil having an odour of tarragon. It has a specific gravity 0.948 to 0.964; optical rotation,  $-7^{\circ} 10'$ ; refractive index, 1.5165; and ester number, 14. Its principal constituent is methyl-chavicol.

**LOVAGE, OIL OF.**—Practically all parts of the plant *Levisticum officinale*, a plant belonging to the natural order *Umbelliferae*, have an aromatic odour and contain essential oils. The roots, on distillation, yield from 0.6 to 1 per cent. of oil calculated on the dried roots. If the root is distilled in the green condition, the essential oil is practically free from resinous matter, but if the roots are first dried, the oil contains much sticky resin. The odour recalls that of angelica. The oil has a specific gravity 1.000 to 1.050; optical rotation,  $0^{\circ}$  to  $+6^{\circ}$ ; refractive index, 1.5390 to 1.5520; and ester value, 175 to 230. The oil contains terpineol, but its other constituents have not been identified with certainty. The high ester value is possibly due to the presence of a lactone rather than to a high proportion of actual esters.

END OF VOL. I.